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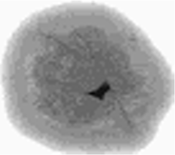

QUALITATIVE ANALYSIS

OUTLINE

OF A SHORT COURSE IN

QUALITATIVE CHEMICAL ANALYSIS

ARRANGED FOR

STUDENTS IN THE COLLEGES OF SCIENCE

OF THE

UNIVERSITY OF CALIFORNIA

BY

W. J. SHARWOOD

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Non METALS −

ACID

MONADS	DYADS	TRIADS	TETRADS	PENTADS	HEXADS
HR Fluorine . 19 F Chlorine . 35.4 Cl Bromine . 80 Br Iodine... 126.5 I HALOGENS Cyanogen * Cy	H_2R Oxygen ....16 O Sulphur ....32 S	R_2O_3 Boron..........11 B RH_3, R_2O_3 Nitrogen........14 N Phosphorus ....31 P	RO Sulphur ....32 S Silicon.........28 Si Carbon.........12 C	R_2O_5 Nitrogen ....14 N Phosphorus ....31 P (Cl, Br, I in Chlorates, etc.)	RO_3 Sulphur .... 32 S
R_2O, R_2S, RCl Hydrogen ... 1 H Silver........108 Ag Mercury(ous)200 Hg (Copper (ous). 63 Cu)	RO, RS, RCl_2 Stannous Tin 118 Sn Lead ....207 Pb Mercury (ic) .200 Hg Copper....... 63 Cu Cadmium ....112 Cd	RH_3, R_2O_3, R_2S_3, (RCl_3) Arsenic (ous)..75 As Antimony(ous)122 Sb	RO_2, RS_2, RCl_4 Stannic Tin ..118 Sn (Platinum ....197 Pt)	R_2O_5, R_2S_5, (RCl_5) Arsenic (ic)... 75 As Antimony (ic). 122 Sb	RO_3 Mn and Cr in Manganic and Chromic Acid
	Nickel ..... 58.5 Ni Cobalt ..... 58.8 Co Ferrous Iron 56 Fe Manganese.. 55 Mn Zinc .... 65 Zn	R_2O_3, R_2S_3, RCl_3 Bismuth.....208 Bi (Gold........197 Au)	RO_2 Lead......... . Pb Manganese......Mn		OCTAD Mn as Mn_2O_7 in Permanganates
		PSEUDO-TRIAD	TETRADS		
Ammonium * (NH_4) Lithium.... 7 Li Sodium....23 Na Potassium .39 K	RO, RCl_2, (RS) Magnesium 24 Mg Calcium.... 40 Ca Strontium.. 87.5 Sr Barium.....137 Ba	R_2O_3, R_2Cl_6 (or RCl_3) Aluminium.........................27 Al Chromium (Chromic Salts).........52.5 Cr Iron (Ferric Salts). ....56 Fe			

+ ~~NON~~-METALS

BASIC

The Symbols HR, RO, etc., show the leading types of compounds formed by the elements under them.

*The group Cy or (CN) acts as an acid radical; (NH_4) as a metal or basic radical; the group (HO)—*hydroxyl*—acts as a monad radical, combining with all oxide-forming elements.

INTRODUCTION.

• • •

QUANTITATIVE Chemical Analysis determines *how much* of any element or body is present in a given substance; Qualitative Analysis, which usually precedes quantitative, shows *of what nature* are the components of the substance. It may be applied—

1. To find out of what a simple substance—e. g. a salt, oxide or metal—consists.

2. To determine all the constituents of a more or less complex mixture.

3. To prove the presence or absence of some particular body in a given substance, as arsenic in food.

The various metals, bases and acids are usually recognized by being brought into some well-known form (e. g. As into $As_2 S_3$), the nature of which can be confirmed by its deportment with acids, etc.

Some skill in manipulation, as well as a knowledge of the principles of Chemistry, is necessary in this work. Before commencing, the student should review his knowledge of General Chemistry and of Nomenclature; he should make himself familiar with the laws governing chemical combination and should understand clearly what is meant by the terms: acid, base, alkali, salts (normal acid or basic), neutralization, saturation, chemical affinity, etc. It is best to commit to memory the valence of the metals and the basicity of the more important acids. See Remsen's Advanced Chemistry, Chaps. I-VI-X.

The *valence* of an element (monad, dyad, triad, etc.) is the number of bonds or units of chemical force it possesses, i. e., the number of atoms of H or Cl that its atom can fix, indicated by the dashes or Roman numerals. Cl' Ba'' Fe'' $(Fe_2)^{VI}$. The valence of a radical or group is the number of its active bonds. $(PO_4)'''$ $(NH_4)'$. Bonds may be positive or negative.

Acids, or hydrogen salts, consist of Hydrogen with a negative element (*Hydracids* as HCl, H_2S) or with oxygen and a negative element (*Oxyacids* as HNO_3), those which are soluble redden litmus. *Thio-acids* contain S in place of O.

Anhydrides are oxyacids minus water, sometimes loosely spoken of as acids:—N_2O_5, SO_3, CO_2. Mono- di- tri- and tetra-basic acids contain 1, 2, 3 and 4 atoms of basic or replaceable Hydrogen to the molecule:—HCl, H_2SO_4, H_3PO_4, H_4SiO_4.

Hydroxides, or hydrates, contain a metal with oxygen and hydrogen. $Zn(HO)_2$. *Bases* are those hydrates or oxides capable of combining with acids. The strongest bases are the alkalis, which turn litmus blue.

Salts are produced, with water, by the mutual action of an acid and a base, the metal of the base replacing the hydrogen of the acid. $ZnCl_2$, $ZnSO_4$. Note that all salts of oxyacids (and also the acids and bases) can be considered, and their formulas written, as the union of a positive with a negative oxide: — $ZnO.SO_3$, $H_2OS.O_3$, $ZnO.H_2O$, putting the more + element first; also that in hydrates water acts as a weak acid, $H(HO)$, and in acids as a weak base, in which H plays the part of a metal:—hydrogen-sulphate, etc.

In *normal* salts the H is exactly replaced by metal (1 atom H for each positive bond):—Na_2CO_3, $ZnSO_4$.

In *acid* salts part of the H remains:—$NaHCO_3$, Na_2HPO_4, $KHSO_4$.

In *basic* salts all the H is replaced by metal and a further quantity of oxide or hydrate enters into the molecule. $ZnSO_4.ZnO$, $PbCO_3Pb(HO)_2$. The terms acid and basic applied to salts do not refer specially to their reaction with litmus, which depends on the relative strength as well as proportion of acid and base; thus Na_2HPO_4, an *acid salt* of a strong base with a weak acid, turns litmus blue, or has an *alkaline reaction.*

The names of salts of hydracids (and binary compounds generally) end in *ide*, oxyacids ending in *ic* and *ous* form salts ending in *ate* and *ite.* Thus hydrosulphuric acid (H_2S) forms sulphides, sulphuric (H_2SO_4) sulphates, sulphurous (H_2SO_3,) sulphites. The terminations *ic* and *ous* or the prefixes *per* and *sub* (or *proto*) indicate greater and less proportions of oxygen or other negative body.

The metals to be studied in this course are given in the lower part of the table on page 15, which indicates the general type of compounds formed by each; roughly speaking any metal in the table is positive to those above it. They are often roughly classified as *alkali metals* (Na, K, Li, (NH_4)), *alkaline-earth metals* (Ba Sr Ca Mg) and *heavy metals*, including all but the above.

Of the acids to be studied the three strong acids, Sulphuric H_2SO_4, Nitric HNO_3 and Hydrochloric HCl are the most important, besides these Phosphoric acid H_3PO_4, Sulphurous H_2SO_3, Carbonic H_2CO_3, Silicic H_4SiO_4, Boric H_3BO_3, Chloric $HClO_3$, Hydrosulphuric H_2S, Hydrofluoric HF, Hydrocyanic HCy, Acetic $H(C_2H_3O_2)$ Oxalic $H_2C_2O_4$ and a few others.

Write the formulae of the following normal salts :—the chloride, nitrate, sulphate and phosphate of potassium, nickel, bismuth and chromium; ferrous and ferric sulphates, stannous and stannic chlorides.

The compounds of the more negative elements (Cl S etc.) with O or H or both act always as acids; the oxides and hydrates of the more positive metals, (the alkalis and alkaline earths) act always as bases; those of some of the intermediate elements act in either sense, forming salts with the strong acids and also with the strongest bases:—$ZnSO_4$, K_2ZnO_2

When an element is capable of more than one degree of oxidation the lower oxide has the more basic properties and that containing most oxygen the more strongly acid.

The stronger acids tend to combine with the stronger bases; i. e. to form salts of the more positive metals.

If a solution containing a salt of a metal be mixed with one containing a salt of an acid which forms an insoluble salt with that metal, then, as a rule, that metal and acid will combine to form a *precipitate*, thus occasionally a weak acid may oust a stronger one from a soluble salt and form an insoluble one. At high temperatures weak non-volatile acids displace stronger but more volatile ones; the same is true of bases.

The *action of mass* must be kept in view in analysis, a large excess of a weak acid, for instance, tending to displace a smaller proportion of a somewhat stronger acid.

The *effect of varying conditions* must also be noted, especially temperature and concentration.

Thus in a cool dilute solution the equation

$$2SbCl_3 + 3H_2S = Sb_2S_3 + 6HCl$$

represents the action that will take place; in a hot concentrated solution this is reversed.

The most important operations in analysis are—the *solution* of a solid; the *digestion* of a solid in a liquid to separate the soluble portion from the insoluble residue; the *precipitation* of a solid from a solution; the *decantation* and *filtration* of a liquid from a precipitate; the *washing* of a precipitate by decantation or filtration, to remove all soluble matter; the *evaporation* of a solution to concentrate it, reduce its bulk or obtain the solid matter it contains as a residue; the *distillation* of volatile liquids and the *ignition*, *sublimation* and *fusion* of solids. See introduction to Fresenius' or Valentin's text-books.

All vessels used must be kept scrupulously clean; they should invariably be cleansed immediately after using, rinsed once or twice with distilled water and left to drain or dry, not wiped.

A *Reagent* is a body which, by reacting chemically with a substance under examination, indicates its composition or separates some of its constituents.

General or group reagents separate several bases or acids (groups) at once; special reagents serve to detect individual metals or acids, or to subdivide groups. Many of them act by precipitating insoluble compounds of the substances sought for.

It is usual to commence by dissolving the substance to be tested, if solid, as chemical action goes on most readily between substances in solution; warming usually facilitates chemical action and hastens the formation and settling of precipitates; many precipitates tend to float on account of entangled gas bubbles or from their fine state of division, but become denser and settle on warming and shaking or stirring.

REAGENTS

Reagents may be roughly classified under four heads.

Solvents, which take up solids to form homogeneous liquids (solutions):—water (forming simple solutions); the stronger acids and solutions of caustic alkalis, forming soluble salts; alkaline sulphides, forming thio-salts; and certain alkaline salts (NH_4Cl, KCN) forming double salts.

Precipitants, throwing down insoluble substances (precipitates) from solutions:—solutions of salts whose acids form insoluble compounds with the metals sought (especially the salts of H and the alkalis, most of which are soluble, those of ammonia having the advantage of being removable by volatilization) and those whose metals form insoluble compounds with the acids sought for.

Oxidizing agents, which tend to add oxygen or a negative element, such as Cl, Br, nitrates and aqua regia.

Reducing agents, tending to remove oxygen or a negative element, as nascent H, H_2S; the more positive metals Zn, Mg, etc., and salts of metals capable of a higher degree of oxidation, $SnCl_2$; in the dry way C and KCN.

REAGENTS USED IN LIQUID FORM.

*Hydrochloric acid, H chloride concentrated and dilute	HCl
*Nitric acid, H Nitrate concentrated and dilute	HNO_3
Sulphuric acid, H sulphate concentrated and dilute	H_2SO_4
*Acetic acid, H Acetate	$HCH_3O_2 = HAc$
*Hydrogen Sulphide water	H_2S
Aqua Regia, Nitro-hydrochloric acid	$(3HCl + HNO_3 = NOCl + Cl_2 + 2H_2O)$
*Ammonium hydrate	NH_4HO
* chloride,	NH_4Cl
* carbonate	$(NH_4)_2CO_3$
* sulphide	$(NH_4)_2S$
sulphide (yellow)	$(NH_4)_2Sx$
oxalate	$(NH_4)_2C_2O_4$
sulphate	$(NH_4)_2SO_4$
acetate	$NH_4C_2H_3O_2$
molybdate	$(NH_4)_2MoO_4$
*Potassium hydrate	KHO
* cyanide	KCN, KCy
* ferrocyanide	K_4FeCy_6
ferricyanide	$K_6Fe_2Cy_{12}$

Potassium thiocyanate (sulphocyanide)	KCNS
Patassium dichromate	$K_2Cr_2O_7$
Sodium hydrate	NaHO
* carbonate	Na_2CO_3
* hydrogen phosphate	Na_2HPO_4
hypochlorite	NaOCl
*Barium hydrate	$Ba(HO)_2$
* nitrate	$Ba(NO_3)_2$
chloride	$BaCl_2$
carbonate (suspended)	$BaCO_3$
*Silver (Argentic) nitrate	$AgNO_3$
Lead (Plumbic) acetate,	$Pb(C_2H_3O_2)_2$
Mercuric chloride	$HgCl_2$
*Stannous chloride	$SnCl_2$
Ferric chloride	Fe_2Cl_6
Ferrous sulphate	$FeSO_4$
Hydrochloroplatinic acid	H_2PtCl_6
Cobalt nitrate	$Co(NO_3)_2$
Chlorine water	Cl
Bromine water	Br
Sulphurous acid water	SO_2
Alcohol	C_2H_5HO
Carbon disulphide	CS_2

H_2S, SO_2 and CO_2 are occasionally used in gaseous form.

REAGENTS USED DRY OR IN SOLID FORM.

Sodium Carbonate (Soda)	Na_2CO_3
Sodium Borate (Borax)	$Na_2B_4O_7 10Aq$
Sodium ammonium hydrogen phosphate (microcosmic salt, phosphor salt)	$NaNH_4HPO_4$

Potassium chlorate	$KClO_3$
nitrate	KNO_3
cyanide	KCN
disulphate	$HKSO_4$ or $K_2S_2O_7$

Carbon and metallic Mg, Zn, Fe, Cu are occasionally used for reducing, also Ag.

The action of the most important general reagents upon solutions containing the various metals is as follows—solutions of moderate concentration and approximately neutral being understood:—

Sodium Carbonate precipitates all the metals, (Arsenic and the alkalis excepted) as carbonates or basic salts, a few as oxides or hydrates (CO_2 escaping). All are decomposed or dissolved by dilute acids. Nearly all salts, soluble or insoluble, boiled with a solution of Na_2CO_3 give up their acid to the sodium which retains it in solution, the base generally remaining as insoluble carbonate. Salts insoluble in acids mostly give up their acid when fused with sodium carbonate, and on extracting with water the acid can be got into solution.

Caustic Alkalis (either potassium hydrate or sodium hydrate can be used) precipitate as oxides or hydrates all the metals except the alkalis, Ca, Ba, Sr and As. An insufficiency often throws down a basic salt at first, converted into hydrate or oxide by an excess or by heating. The precipitates of Sb Sn Pb Zn Cr and Al are soluble in an excess of this precipitant, careful neutralization with acids reprecipitates them. Those of Ag Cu Mg Cd Ni Co Zn dissolve in either NH_4HO, NH_4Cl or in both. All combine with dilute acids.

Ammonic hydrate precipitates as hydrates, oxides, or as basic or metallammonium salts all the metals except the alkalis, Ba Sr Ca and As (Mg partially). The precipitates of Ag Cu Cd Ni Co Zn readily dissolve in excess, those of Cr and Al slightly; those of Mn and Mg, also Zn Ni Co dissolve in NH_4Cl and some other ammonic salts. All are dissolved or decomposed by acids.

Hydrogen sulphide gas is prepared by acting on ferrous sulphide with dilute sulphuric acid, the *solution* by passing this into cold boiled water. From acid solutions it precipitates Ag

Cu Pb Hg Bi Cd As Sb Sn only as sulphides; from neutral or slightly alkaline solutions or solutions of acetates Co Ni Zn Mn Fe are also thrown down more or less completely. From oxidizing solutions white finely-divided sulphur is thrown down.

Ammonic sulphide (prepared by half saturating the hydrate with H_2S, exposed to light it becomes yellow and contains polysulphide) precipitates all the heavy metals from neutral or acid solutions, Cr and Al as *hydrates* the rest as sulphides: those of As Sb Sn dissolve readily in an excess of yellow ammonic sulphide, those of Ni and Cu slightly. Hot nitric acid attacks all but HgS, nitrates, free sulphur and NO being generally formed; those of Pb Sn Sb and As are more or less oxidized to $PbSO_4$, $SnO(HO)_2$, Sb_2O_5, As_2O_5.

Sodium phosphate precipitates all metals but the alkalis and As as phosphates, soluble in acids.

Potassium Cyanide precipitates most heavy metals as cyanides, many being soluble in excess as double cyanides.

When using any reagent make it a point to learn its name and formula, and consider what effect it can possibly have on the solution or substance under examination, i. e., what compounds it can possibly form with the bodies present under the present conditions.

Formulæ are used throughout these instructions to indicate solutions of the corresponding substances, but in speaking of reagents the *names* should always be used.

Add reagents drop by drop from the bottle or with a pipette, noting the effect of each addition. A single drop of some produces a visible result, while others under certain conditions may require to be used in large quantity. For instance, take 5 ccs of a solution of ferric chloride, add half its bulk of any strong acid and a little water; divide in two parts; to one add one drop of potassium ferrocyanide, and to the other ammonia water, drop by drop, with constant stirring. In the latter case no result is seen till all the free acid is neutralized.

An *excess* of a reagent means not an indefinite amount but rather more than enough to insure a complete reaction; in most cases a slight excess is proper.

Dilute acids are to be understood unless the concentrated are mentioned, and distilled water is used in all dilutions, etc.

In using a reagent bottle never lay the stopper down, but hold it between the fingers till it can be replaced; reagents once poured from a bottle are not to be returned.

NOTE—All highly colored precipitates can be neatly obtained by putting one drop of the solution to be tested on a piece of filter paper with a glass rod, and adding a drop of reagent; the colored spot can be tested as to solubility, etc., with a drop of acid; if dissolved it disappears.

White or other precipitates can be seen by putting the two drops side by side on a clean glass plate and mixing with glass rod.

BLOWPIPE TESTS

Blowpipe tests made "in the dry way" are very useful as being rapidly performed and requiring but small quantities of the substance, usually in the solid state.

The blowpipe is used with an oil lamp, or candle, or a Bunsen burner with airholes closed, the flame about 1½ inches high.

The *oxidizing flame* (OF) is produced by holding the blowpipe nozzle very near the burner and well into the edge of the flame; on blowing gently a blue non-luminous cone is produced; the hottest point is just outside the tip of this inner blue portion, and all beyond this is *oxidizing*.

The *reducing flame* (RF) is formed by holding the nozzle a little higher and just at edge of flame; all within the blue is *reducing*.

Borax beads are made by taking up a little borax ($Na_2B_4O_7Aq$) in a circular loop, 1/8 inch in diameter, at end of a platinum wire, and heating till it fuses to a clear glass; this dissolves most metallic oxides and is colored by some, the colors in OF and RF varying.

Beads of sodium metaphosphate ($NaPO_3$) are formed in the same way by heating microcosmic salt ($NaNH_4HPO_4Aq$).

Tests on charcoal are made with a slip of coal about 1x1x4 inches. The assay is placed in a cavity near one end and the flame directed upon it while held in an inclined position; in the OF many substances form *sublimates* of oxides on the face, the distance from assay being a measure of the volatility; in RF many oxides are reduced to metal, more readily if mixed with Na_2CO_3 or KCN.

Closed tubes are made of hard glass about 3 inches long by 3/16 in bore, closed at one end; if held aslant and heated volatile substances placed in them form sublimates, and decomposable ones may give off water or gases recognizable by various tests.

Flame tests are made by taking up a solid or strong solution on a platinum wire (previously cleaned by dipping in HCl and igniting) and holding in a Bunsen or colorless blowpipe flame; some volatile substances then produce characteristic colors, some only on moistening with HCl or conc. H_2SO_4.

LABORATORY WORK

Treat the powder supplied (No. 1) as directed in sheet of special instructions.

Then, having read carefully the preceding pages, work through the *reactions of the metals*, use the solutions prepared in the laboratory which contain ½, 1 or 2 per cent. of metal. A very small quantity, not over 2 or 3 ccs, should be taken in a perfectly clean test tube for each test, and the reagent added drop by drop. When a precipitate is to be tested as to solubility, etc., with other reagents, it must be *washed*, i. e. allowed to settle (settling is promoted by first shaking and warming), the supernatant liquid decanted off, a little water added and, after shaking and settling, also poured off; the precipitate is now fairly pure. If not washed the effect of reagents may be considerably modified by the action of the liquid adhering to it. When several tests have to be made on one precipitate a larger amount, 6 or 8 ccs, may be taken, and the washed precipitate divided by shaking up with water and pouring into clean test tubes.

After working through the reactions of each metal write the equations corresponding, in all cases in which a definite chemical compound is produced, as indicated by the formula. The reactions involved are in nearly all cases simply the substitution or exchange of atoms or groups for one another, with, in a few cases, oxidizing or reducing effects. Only the more important tests, and such as serve to effect separations, are here given. Very many others will be found, with detailed equations, in Prescott and Johnson's book, which is recommended for reference.

The abbreviations used are pp. for precipitate; sol., soluble; insol., insoluble; reppd., reprecipitated; dil., dilute; conc., concentrated.

After completing a group it will be found a valuable exercise to tabulate the effects of the more important reagents on the metals of the group, and to devise methods of separating the individual metals from one another.

REACTIONS OF THE METALS.

The metals are here grouped according to their analytical relations. The groups do not generally coincide with those based on the periodic law.

The symbol, valence and atomic weight are given immediately after the name of each metal, together with the compounds most suitable for performing the tests mentioned.

SILVER GROUP.

Ag, Pb, Hg′ (mercurous salts).

The chlorides of this group are white and insoluble in water or nearly so, the sulphates difficultly soluble. The sulphides are black, insoluble in cold dilute acids. Their soluble salts with strong acids redden litmus.

SILVER Ag′ 108. Use $AgNO_3$.

Heated on charcoal with Na_2CO_3 all compounds yield white beads of metal, difficultly fusible not oxidizable.

HCl (or soluble chlorides) pps white curdy AgCl, darkened by sunlight; insol in acids, unless added in great excess; fuses when heated; sol NH_4OH or KCN, reppd by acidulating with $H NO_3$, slightly soluble in solutions of chlorides (NaCl etc.).

$H_2 S$ pps black $Ag_2 S$, insol in acids, sol hot HNO_3.*

$(NH_4)_2 S$ pps $Ag_2 S$, insol in excess difficultly, sol KCN.

KHO pps brown Ag_2O insol excess.

$NH_4 HO$ pps Ag_2O, readily sol in excess or in NH_4 salts, No pp in weak solution.

KCN pps while AgCN, sol in excess or in NH_4HO; decomposed by hot HNO_3 or by ignition, otherwise like AgCl.

Many other reagents throw down precipitates from silver solutions, but all of them dissolve in KCN and very many in NH_4,HO or HNO_3.

---

* Most of the precipitated sulphides form with hot nitric acid a soluble nitrate and leave an insoluble residue of sulphur, often black and plastic, part of the acid being reduced to lower oxides of nitrogen.

LEAD Pb″ 207. Use Pb $(NO_3)_2$, or Pb $(C_2H_3O_2)_2$.

Heated on Charcoal with Na_2CO_3 in inner flame all compounds yield beads of metal, malleable and so soft as to mark paper. A sublimate of oxide forms rather near assay, orange to yellow while hot, yellow to white cold, volatile, can be driven about by flame coloring it blue (compare Bi).

HCl (or any soluble chloride) pps, incompletely, white $PbCl_2$ from strong solutions only (sol in 130 parts cold or 33 of boiling water, crystallizes out on cooling), NH_4HO converts this into white PbClHO insol even in hot water.

H_2S pps black PbS insol in alkalis or cold dilute acids (see under Copper Group).

H_2SO_4 pps white $PbSO_4$ insol in excess, somewhat sol in dil HCl or HNO_3, ppd completely on adding alcohol; sol in KHO or ammonium acetate $(NH_4C_2H_3O_2)$.

K_2CrO_4 pps yellow $PbCrO_4$, sol KHO, insol in acetic acid.

KHO pps white basic salt, sol in excess as K_2PbO_2 (plumbite).

NH_4HO pps white basic salt, insol in excess (no pp from acetate).

KI pps yellow PbI_2, sol in excess or in hot water.

MERCUROUS COMPOUNDS, Hg′ or $(Hg_2)^{II}$ 200. Use $Hg_2\ (NO_3)_2$.

Heated in a closed tube all mercury compounds either yield a sublimate ($HgCl_2$) or are decomposed (HgO), yielding a mirror of metal.

Heated with dry Na_2CO_3 in a closed tube all compounds give a mirror and globules of metal.

Bright metallic copper placed in any mercury solution reduces metallic Hg and appears silvery on rubbing; metal removed by heating.

From Mercurous solutions:

Water added in excess pps basic salts, e. g. $HgOHg_2(NO_3)_2$, sol in HNO_3.

HCl (or a sol chloride) pps white Hg_2Cl_2, insol in dil acids, sol in aqua regia or boiling HNO_3, slightly in boiling HCl. NH_4HO blackens it, forming insoluble NH_2Hg_2Cl.

KHO pps black Hg_2O insol in excess

NH_4HO gives black precipitates.

H_2S pps black Hg_2S (forming $Hg + HgS$) insol in dilute acid, insol in hot dil HNO_3, hot conc HNO_3 forms white insol compound.

$(NH_4)_2S$ pps Hg_2S insol in excess.

$SnCl_2$ pps grey metallic Hg.

Oxidizing agents, Cl or Br, conc HNO_3 or aqua regia oxidize mercurous to mercuric compounds (see under Copper Group).

THE ALKALI METALS.

Na, K, Li, NH_4.

Practically all their single salts are soluble in water; all are colorless unless combined with colored acids. Their salts with weak acids turn litmus blue. The spectroscope and flame tests give the readiest means of determining them. All are monads; ammonium is a hypothetical metal.

SODIUM Na′ 23. Use NaCl.

Flame test: Platinum wire dipped in solution and held at base of Bunsen flame colors it strongly and persistently yellow. Dilute solutions must be evaporated down; solids should be moistened with HCl before testing.

POTASSIUM K' 39. Use KCl or KNO_3.

Flame test: K compounds color flame purplish; seen through a thick blue glass color is red-violet, Na color being cut off.

$PtCl_42HCl$ gives a yellow pp $PtCl_42KCl$; insol in alcohol or ether.

LITHIUM Li' 7. Use Li_2CO_3.

Flame test: Carmine, very persistent.

AMMONIUM NH_4'. Use NH_4Cl.

In closed tubes all compounds are volatile or give off NH_3.

Boiled with KHO, or heated with lime ($Ca(HO)_2$) all compounds give off ammonia NH_3, with characteristic odor, the gas turning red litmus blue, and turmeric brown.

METALS OF THE ALKALINE EARTHS.

Mg, Ba, Sr, Ca.

The hydrates of these metals turn litmus blue; their salts with strong acids are neutral to litmus; all are dyads: Heated on charcoal their salts leave in most cases infusible residues which glow on strong ignition. All are precipitated by sodium phosphate, but not by ammonium sulphide.

MAGNESIUM Mg'' 24. Use $MgSO_4$ or $MgCl_2$.

Magnesium differs from the lime group in many ways. The sulphate is soluble in water, the carbonate in NH_4Cl; the oxide is almost insoluble in water (1 in 500), but soluble in NH_4Cl; the salts do not color flame.

Na_2HPO_4, pps white $MgHPO_4$, soluble in acetic and other acids, insol in alkalis; in presence of ammonic salts a

white pp of $MgNH_4PO_4$ is formed, which is crystalline from moderately dilute solutions; sol in acetic acid, insol in ammonia.

K HO pps white $Mg(HO)_2$ sol in NH_4Cl; in presence of ammonic salts excess of K HO must be added and boiled to produce a pp.

NH_4HO pps white $Mg(HO)_2$ partially, sol in NH_4Cl as $MgCl_2 . 2 NH_4Cl$.

THE LIME GROUP.

Ba, Sr, Ca.

Volatile compounds of these metals color the flame strongly. Some compounds (e. g. Ba SO_4) only react after being reduced on charcoal and treated with HCl.

Soluble carbonates, or CO_2 in presence of alkali, precipitate them as carbonates, almost insoluble in NH_4Cl, but excess of CO_2 forms soluble bicarbonates, $CaH_2(CO_3)_2$ etc.

Pure caustic alkalis and ammonia give no precipitates, but if any carbonate or sulphate is present or if exposed to air a precipitate forms. Sulphates of Ba and Sr are insoluble in water, $CaSO_4$ dissolves in about 400 parts, more readily in acids.

BARIUM Ba^{II} 137. Use $BaCl_2$.

Barium compounds color flame yellowish green.

$(NH_4)_2\ CO_3$ pps white $BaCO_3$, insol in NH_4Cl, sol in dil HCl, HNO_3 or acetic acid.

H_2SO_4 and sulphates (as $CaSO_4$) pp white $BaSO_4$ insol in alkalis and dilute acids.

K_2CrO_4 pps yellow $BaCrO_4$ insol in acetic acid, sol HCl. The chloride and nitrate are insoluble in alcohol.

STRONTIUM Sr^{II} 87. Use $SrCl_2$.

Strontium compounds color flame crimson (compare Li and Ca).

$(NH_4)_2CO_3$ pps white $SrCO_3$ insol in NH_4Cl, sol in dil HCl, HNO_3 or acetic acid.

H_2SO_4 and sol sulphates pp white $SrSO_4$ slightly sol in HCl, insol in strong solution of $(NH_4)_2SO_4$.

The chloride is soluble, the nitrate insoluble in alcohol.

CALCIUM Ca^{II} 40.

Calcium compounds color flame red (compare Sr and Na).

$(NH_4)_2 CO_3$ pps white $CaCO_3$ insol NH_4Cl, sol in dil HCl, HNO_3 or Acetic acid.

H_2SO_4 and sol sulphates (as $(NH_4)_2SO_4$) pp white $CaSO_4$ from strong solutions, soluble in a hot strong solution of $(NH_4)_2SO_4$ somewhat sol in water, readily in HCl; insol in alcohol which completes precipitation.

$(NH_4)_2C_2O_4$ pps white CaC_2O_4 insol in acetic acid, sol in HCl; Ba and Sr oxalates being sol in acetic acid.

The chloride and nitrate dissolve in alcohol.

IRON GROUP.

Al, Cr, Fe, Mn, Zn, Ni, Co.

The salts of all these metals, with strong acids, dissolve in water and redden litmus.

PSEUDO-TRIAD METALS; FORMING SESQUIOXIDES.

Al, Cr in Chromic salts, Fe in Ferric salts.

Forming oxides and chlorides of the type R_2O_3, R_2Cl_6; their sulphates combine with those of the alkalis to form *alums*, e. g. $Al_2K_2(SO_4)_4\ 24H_2O$. Their salts tend to decompose when heated, losing acid; the oxides or hydrates if heated strongly become insoluble in acids. Alkaline carbonates Na_2CO_3, or $(NH_4)_2CO_3$ precipitate them as hydrates, most of the CO_2 escaping; shaken up with $BaCO_3$ the same action takes place.

ALUMINIUM. Al^{IV} or $(Al_2)^{VI}$ 27. Use $Al_2(SO_4)_3$ or ammonia alum $Al_2(NH_4)_2(SO_4)_4$.

Compounds are colorless; heated upon charcoal they leave white infusible residues; if these are cooled, moistened with a weak solution of cobalt and again ignited they form sky-blue $CoOAl_2O_3$, Thenard's blue.

NH_4HO pps whitish gelatinous $Al_2(HO)_6$ sol in acids and KHO, almost insol in NH_4HO and NH_4Cl; best seen after heating and allowing to stand a few minutes.

KHO pps $Al_2(HO)_6$ very readily sol in excess as $K_2OAl_2O_3$ (aluminate), reppd by NH_4Cl or on *careful* neutralization (as by HCl or CO_2), but not by simple boiling (compare Zn).

$(NH_4)_2S$ pps $Al_2(HO)_6$, H_2S escaping.

H_2S gives no pp.

CHROMIUM, CHROMIC SALTS Cr^{IV} or $(Cr_2)^{VI}$ 52.5. Use Cr_2Cl_6 or Chrome Alum $Cr_2K_2(SO_4)_4$.

Most chromic salts and solutions have a green or violet color. All compounds give green beads in borax in OF and RF. Fused on Platinum foil with four volumes of dry Na_2CO_3 and one of $KClO_3$ they are oxidized to yellow alkaline chromate $Na_2Cr^{VI}O_4$; this dissolves in water, and, on acidulating with acetic acid and adding two drops of lead acetate solution, gives a yellow pp. $PbCrO_4$.

NH_4HO pps greenish $Cr_2(HO)_6$ slightly sol in excess (pink); reppd by boiling or by NH_4Cl; sol in acids and in KHO.

KHO pps $Cr_2(HO)_6$ sol in excess (green); reppd on *long* boiling (more readily if first diluted) or on adding NH_4Cl.

$(NH_4)_2S$ pps $Cr_2(HO)_6$, H_2S escaping; H_2S gives no pp.

CHROMIC ACID, H_2CrO_4, and chromates (see also under Acids). Use $K_2Cr_2O_7$.

H_2S, after acidulating with HCl, pps S, forming Cr_2Cl_6, solution turning green; other reducing agents with HCl yield green Cr_2Cl_6, giving reactions as above.

Alkalis give no pp with chromates before reduction.

Chromous salts are rarely met with, and are readily oxidized to chromic.

IRON (FERRIC COMPOUNDS) Fe^{IV} or $(Fe_2)^{VI}$ 56. Use Fe_2Cl_6.

Heated on charcoal all iron compounds leave dark residues, magnetic on cooling. Borax bead is yellow to red while hot, yellowish cold in OF, greenish in RF.

Ferric compounds and solutions are generally yellow or reddish brown. They are reduced to the ferrous state by reducing agents: H_2S, SO_2, $SnCl_2$, and Zn Cd or Fe with HCl are most used. See reactions of Ferrous compounds.

NH_4HO precipitates red-brown $Fe_2(HO)_6$ or $Fe_2O_3H_2O$, insol in excess or in NH_4Cl, sol in HCl. With H_2S or $(NH_4)_2S$ this yields black $2FeS + S$.

KHO pps $Fe_2(HO)_6$ insol in excess, pp always retains alkali.

H_2S pps finely divided sulphur, forming a ferrous salt and removing yellow color.

$(NH_4)_2S$ pps black *ferrous* sulphide mixed with sulphur $2FeS + S$, insol in excess; sol in dil HCl *leaving insoluble sulphur.* + [illegible]

K_4FeCy_6 pps 'Prussian blue' $Fe_4(FeCy_6)_3$; decomposed by alkalis or conc acids; acidulate with acetic acid or HCl before testing.

$K_6Fe_2Cy_{12}$ gives a green or brown color but no blue pp on acidulating; addition of a reducing agent (a drop of $SnCl_2$) gives blue color.

KCNS after acidulating gives red color due to soluble $Fe_2(CNS)_6$; $HgCl_2$ removes color.

Na_2HPO_4 pps yellowish white $Fe_2(PO_4)_2$ almost insol in acetic acid, sol HCl. Precipitation is complete in presence of alkaline acetate ($NH_4C_2H_3O_2$). The phosphates of Fe^{IV} Al and Cr are very stable; if a solution containing ferric iron and also P_2O_5 or a phosphate dissolved in acid, be neutralized by NH_4HO, $Fe_2(PO_4)_2$ will be thrown down with the $Fe_2(HO)_6$, and if sufficient iron be present all the P_2O_5 will combine with it in preference to other metals, forming basic ferric phosphate.

$NH_4C_2H_3O_2$ (ammonic acetate) added to a nearly neutral solution and boiled, pps brown basic ferric acetate, insol in hot water. In presence of phosphates the basic acetate carries down all the P_2O_5 provided sufficient iron be present.

Cr and Al behave like Fe^{IV} in regard to phosphates and alkaline acetates, $Al_2(PO_4)_2$ is slightly more soluble in acetic acid than the others. The Cr pps are greenish, those of Al whitish, like the hydrates. The basic acetate method separates them from nearly all other metals. The precipitated hydrates, phosphates and basic acetates of these metals are gelatinous or slimy and should be filtered hot. Towards KHO and $(NH_4)_2S$ they act much like the hydrates and can be separated in the same way.

The presence of organic matter, especially sugar and certain acids (citric) prevents the precipitation of these metals by ammonia and retards the action of other reagents; it must therefore be removed in analysis by evaporating to dryness with HNO_3 and heating.

DYAD METALS OF THE IRON GROUP.

Fe^{II}, Mn, Ni, Co, Zn.

All are precipitated by $(NH_4)_2S$ as sulphides; exposed to air these tend to oxidize to sulphates; Na_2HPO_4 precipitates them as phosphates, somewhat soluble in NH_4Cl; the hydrates are all soluble in NH_4Cl, and with $(NH_4)_2S$ or H_2S yield sulphides insoluble in NH_4Cl. Alkaline carbonates precipitate carbonates having solubilities similar to the respective hydrates The chlorides and nitrates are not precipitated by $BaCO_3$.

IRON (FERROUS COMPOUNDS) $Fe^{II}56$. Use $Fe^{II}SO_4$. Ferrous salts and solutions are colorless or pale green. They are oxidized to ferric salts by oxidizing agents, e. g. Cl or Br water, boiling with a few drops of conc HNO_3 or simple exposure to the air; solutions usually contain some ferric salt.

NH_4HO pps, incompletely, dull green $Fe(HO)_2$ (*pure* $Fe(HO)_2$ is white); by absorption of O this darkens to red-brown $Fe_2(HO)_6$; pp is somewhat sol in NH_4Cl.

KHO pps dull green $Fe(HO)_2$ insol in excess.

$(NH_4)_2S$ pps black FeS, insol in excess or in NH_4Cl, completely soluble in dil HCl. FeS oxidizes easily to $FeSO_4$.

K_4FeCy_6 pps light blue $K_2Fe''Fe''Cy_6$, insol in dilute acids; oxidizes readily to dark Prussian blue.

$K_6Fe_2Cy_{12}$ pps Turnbull's blue $Fe_3''Fe_2^{IV}Cy_{12}$, insol in dilute acids; alkalis decompose these pps; solutions should be made acid with acetate (or HCl) before testing.

KCNS usually gives a red color, due to admixed Ferric salt; no reaction with *pure* ferrous salts.

MANGANESE (MANGANOUS SALTS) Mn''55. Use $MnCl_2$.

Compounds are mostly pink; some become brown owing to a tendency to form manganic compounds.

Fused on Platinum foil with 3 or 4 parts dry Na_2CO_3 and 1 of $KClO_3$ all compounds yield a *green* manganate (Na_2MnO_4); dissolving in water to purple permanganate, $Na_2Mn_2O_8$, MnO_2 being precipitated; color removed by alcohol and reducing agents.

Borax bead amethyst in OF, colorless RF.

NH_4HO pps white Mn $(HO)_2$ insol in excess.

Soluble in acids or NH_4Cl, readily oxidized, on exposure, to dark brown $Mn_2(HO)_6$, insol in NH_4Cl.

The NH_4Cl solution oxidizes on standing, $Mn_2(HO)_6$ falling out.

KHO pps white Mn $(HO)_2$.

$(NH_4)_2S$ pps MnS pink or greenish yellow. Soluble in dilute acids, even *acetic* (separation from rest of group).

Manganic compounds and higher oxides are reduced to manganous by heating with HCl.

	NICKEL Ni″ 58.5	COBALT Co″ 59
Use a solution of	$NiSO_4$	$CoCl_2$ or $Co(NO_3)_2$
Note color, most salts are	Green	Rose colored
Add HCl, evaporate to dryness	Becomes yellow	Becomes blue
Test in Borax bead	Brown OF, turbid RF	Blue
KHO pps { insol in excess	Apple green $Ni(HO)_2$	Blue basic salt, or rose $Co(HO)_2$
KHO pps { sol in NH_4HO	Not oxidized on exposure	Oxidizes to brown $Co_2(HO)_6$
NH_4HO gives slight pp. pp is sol in N	Green, sol in excess (blue) NH_4 salts and none forms	Bluish, sol in excess (red) in acid solutions
Na_2CO_3 } $(NH_4)_2Co_3$ } pps (sol in NH_4 salts)	Green	Peach colored
$(NH_4)_2S$ pps.	Black NiS. Somewhat sol in excess (dark brown); reppd on boiling or by acetic acid	Almost insol in excess
In cold dilute HCl or acetic acid; the sulphide is	Insoluble	Insoluble
In HNO_3 or aqua regia	Soluble	Soluble

H_2S gives no pp from acid solution; from acetates or alkaline solutions pps black sulphide.

ZINC Zn″ 65. Use $ZnCl_2$ or $ZnSO_4$

Compounds are mostly white, the sulphide included.

Heated on charcoal most compounds give a whitish residue and in R F all wield a sublimate (ZnO), which is white cold, yellowish while hot, glowing with a peculiar greenish light, *not volatile in OF*; if cooled, moistened with dilute $Co(NO_3)_2$ and again heated, *yellow green* Co_2O_3ZnO is left.

$NH_4.HO$ pps white $Zn(HO)_2$ sol in excess, reppd on boiling sol in NH_4Cl.

KHO pps $Zn(HO)_2$ sol in excess, $ZnOK_2O$, (zincate); reppd by dilution or boiling, not by NH_4Cl.

$(NH_4)_2S$ pps white ZnS insol in excess, in alkalis or NH_4Cl, sol in dil HCl (all other salts dissolve in KHO.)

H_2S gives no pp with acid solutions except acetates, but pps ZnS from alkaline solutions.

Separations. The sesquioxide metals can be separated from the dyads (1) readily but incompletely by NH_4 Cl + NH_4 HO, more perfectly (2) as basic acetates or (3) by $BaCO_3$ in absence of H_2SO_4. Ni and Co maybe separated by the insolubility of their sulphides in dilute HCl, Mn by the solubility of MnS in acetic acid, Zn from other dyads by the solubility of the hydrate in KHO. Cr, Mn, Co and Fe can be readily detected by special tests without separation.

COPPER GROUP.

Cu Hg″ Pb Bi Cd.

Solutions of salts of this group have an acid reaction; H_2S precipitates them all as sulphides; insoluble in dilute acids. Alkaline carbonates precipitate their basic carbonates and sodium phosphate the normal phosphates.

COPPER (CUPRIC SALTS) Cu″63. Use $CuSO_4$.

Solutions generally are blue or green, with nauseous taste. Copper compounds moistened with HCl color flames vivid blue-green. Borax bead is green hot, bluish cold, in OF; in RF opaque-red on cooling. On charcoal in RF with Na_2CO_3 most compounds are reduced to red metal, difficultly fusible.

KHO pps bluish $Cu(HO)_2$, on boiling forms black CuO; insol in excess, except in presence of organic matter; sol in NH_4HO (blue) and in KCN (colorless).

NH_4HO pps bluish basic salt, sol in excess (azure blue) as $CuSO_4\,4NH_3Aq$; KCN removes this color. H_2S added to blue solution pps black CuS, but does not affect the colorless K_2CuCy_4.

H_2S pps brownish black CuS, insol in dil HCl or H_2SO_4, sol in hot dil HNO_3 and in KCN.

$(NH_4)_2S$ pps CuS, slightly sol in excess, especially of the yellow salt, reppd by acids, liver-colored.

Na_2CO_3 pps greenish basic carbonate $Cu_2(HO)_2CO_3$, black CuO on boiling, sol KCN.

K_4FeCy_6 pps brownish Cu_2FeCy_6 insol in acetic acid, decomposed by KHO.

Bright Metallic Iron reduces red metallic Cu and is plated by it.

Cuprous salts are rarely met with and are easily oxidized to cupric.

MERCURY, MERCURIC COMPOUNDS, Hg″. 200 Use $HgCl_2$ or $Hg(NO_3)_2$.

From *mercuric* solutions:—

HCl gives no pp.

Water pps the nitrate and oxy-salts, but not $HgCl_2$, as white basic salts or yellowish HgO.

KHO or *Na_2CO_3* pps brown basic salt; on heating, yellow HgO; insol in excess.

NH_4HO pps white mercuric-ammonium salt; insol in excess; sol HCl.

H_2S gives a pp, *white at first* (Hg_2SCl_2, etc.), which, with more H_2S, becomes yellow-brown and finally *black* HgS; insol in acids, even in boiling HNO_3 (strong HNO_3 slowly forms white insoluble $Hg_2S(NO_3)_2$); insol in NH_4HO or $(NH_4)_2S$; somewhat sol in $Na_2S+NaHO$; *sol in aqua regia.*

$(NH_4)_2S$ gives same white pp, finally black HgS; insol in excess.

KI pps orange or red HgI_2; sol in excess.

$SnCl_2$ pps white Hg_2Cl_2 at first; larger quantities reduce this completely to grey metallic Hg.

Mercuric solutions are highly corrosive, attacking many metals (e. g. Ag Fe) and being reduced to mercurous salts or to metal. (See also under Silver Group.)

CADMIUM Cd″ 112. Use $Cd(NO_3)_2$.

On charcoal in RF compounds give a brown sublimate, very volatile and transient.

KHO pps white $Cd(HO)_2$; insol in ex; sol in KCN.

NH_4Ho pps white $Cd(HO)_2$; sol in ex; sol in KCN.

H_2S pps these akaline solutions (compare Ca).

H_2S pps yellow CdS finely pulverulent, tends to pass through filter; insoluble in *very* dilute acids; sol on warming and in H_2SO_4; insol in alkalis, alkaline sulphides and in KCN.

$(NH_4)_2S$ pps CdS; insol in excess.

Na_2CO_3 pps white $CdCO_3$; insol in excess; sol in KCN.

LEAD Pb″ 207. See also under Silver Group.

Lead chloride is somewhat soluble in water, hence some lead always remains in solution after the silver group is precipitated.

H_2S pps black PbS insol in alkalis or cold dil acids, sol in hot dil HNO_3 as $Pb(NO_3)_2$, S separating; conc HNO_3 oxidizes it to white insoluble $PbSO_4$. Strong HCl and H_2SO_4 convert it into *chloride or sulphate.*

From solutions strongly acid with HCl a brick-red pp. Pb_2SCl_2 (sulpho-chloride) may be thrown down at first.

$(NH_4)_2S$ pps PbS insol in excess.

Na_2CO_3 pps white basic carbonate, insol in KCN.

BISMUTH Bi‴ 208. Use $Bi(NO_3)_3 + HNO_3$.

Heated on charcoal Bi compounds are very easily reduced to fusible beads of *brittle* metal; sublimate (Bi_2O_3) yellow-brown.

Roy Ravone Rogers

hot, white to yellow cold; volatile, exactly like lead, but does not color flame.

Bismuth salts are soluble in water only in presence of acid.

Water, in excess, precipitates white basic salts (salts of bismuthyl BiO), $BiONO_3$, etc. The oxychloride, BiOCl, is one of the least soluble of these, hence the addition of a little HCl facilitates precipitation.

The basic salts dissolve in HCl or HNO_3, not in tartaric acid (comp Sb).

KHO and NH_4HO pp white BiOHO, becoming yellow; insol in excess, sol in dilute HCl.

H_2S pps brown-black Bi_2S_3; insol in dilute acids, alkalis or KCN; sol in hot dilute HNO_3.

$(NH_4)_2S$ pps Bi_2S_3, insol in excess.

$Sn''Cl_2$ + excess of *KHO* ($= K_2Sn''O_2$) reduces black Bi_2O_2.

K_2CrO_4 pps yellow basic chromate $Bi_2O(CrO_4)_2$, sol in acid *insol in KHO.*

Na_2CO_3 pps white $(BiO)_2CO_3$, insol in KCN.

ARSENIC GROUP.

As Sb Sn.

These are all capable of two degrees of oxidation.

They are the least positive of the metals. As having most of the characterics of a non-metal, it and Sb combining directly with H. The oxides of As and Sb act as acids in nearly all cases, that of Sn frequently. All form chlorides, but not carbonates; As and Sb form no nitrates, and As no sulphate. The chlorides have an acid reaction and are decomposed on addition of water. Their salts with alkali metals have an alkaline reaction.

H_2S precipitates the acid, but not the strongly alkaline solutions. They are distinguished by the readily solubility of the sulphides in caustic potash, yellow ammonium sulphide, or in sodium sulphide. The hydrates also dissolve in caustic potash.

TIN, Sn″ or ^{IV} 118.

On charcoal, fused in RF with Na_2CO_3 or KCN all compounds yield small beads of fusible white metal and a coating close to assay, white cold, yellowish hot, nonvolatile; moistened with $Co(NO_3)_2$ and ignited this becomes bluish green.

STANNOUS SALTS, Sn″. Use $SnCl_2 + HCl$.

All are strong reducing agents and in air become oxidized to stannic compounds, more rapidly by Cl or nitric acid.

Alkaline solutions, *Stannites*, on careful neutralization with HCl give precipitates of $Sn(HO)_2$; soluble on further addition of HCl or in KHO.

The following reactions take place in solutions rendered acid by HCl.

H_2S pps dark brown SnS; insol in dilute HCl, NH_4HO $(NH_4)_2CO_3$ or colorless $(NH_4)_2S$—monosulphide; readily sol in KHO or yellow $(NH_4)_2S_X$—polysulphide; reprecipitated on acidulating with HCl as SnS and SnS_2 respectively; soluble in moderately strong HCl on heating.

$(NH_4)_2S$ pps SnS; sol in excess of the yellow sulphide, as *thiostannate* $SnS_2(NH_4)_2S$.

KHO pps white $Sn(HO)_2$; sol in excess, as K stannite SnO K_2O.

NH_4HO, *$(NH_4)_2CO_3$* or *Na_2CO_3*, pps white $Sn(HO)_2$; insol in excess.

$HgCl_2$ is precipitated as white Hg_2Cl_2 or if a small quantity be added, as grey Hg.

Metallic Zn pps grey metallic Sn; sol in HCl.

Water, in excess, gives a milky white basic pp, sol in HCl.

Copper does not reduce stannous salts.

STANNIC SALTS, Sn^{IV}. Use $SnCl_4$.

Alkaline solutions, *Stannates*, are precipitated on careful neutralization with HCl, as $SnO(HO)_2$.

In solutions made acid with HCl:

H_2S pps (more readily on heating) yellow SnS_2; soluble in KHO and $(NH_4)_2S$, reprecipitated on acidulation, otherwise like SnS.

$(NH_4)_2S$ pps yellow SnS_2; soluble in excess, as thiostannate.

KHO, or *Na_2CO_3* pps white stannic acid $SnO(HO)_2$; sol in excess of KHO as K stannate, or in HCl as $SnCl_4$.

NH_4HO or *$(NH_4)_2CO_3$*, same pp; insol in excess.

Boiling after dilution, and especially on adding a neutral salt of an alkali, as Na_2SO_4, pps metastannic acid $Sn_5O_5(HO)_{10}$; insol in acids; sol in KHO.

$HgCl_2$ gives no pp.

Metallic Zinc pps metallic tin; this dissolves in warm HCl to form stannous salts, giving a pp with $HgCl_2$, etc.

Metallic Cu reduces to $SnCl_2$, but not to metal.

ANTIMONY Sb''' or ^{V} 122.

Antimony tends to form basic salts, compounds of antimonyl SbO. The tartrate is the only salt of Sb with an acid that is not decomposed by water.

Heated on charcoal in inner blowpipe flame with Na_2CO_3 or KCN, Sb compounds are reduced to beads of grey brittle fusible metal, easily oxidized, forming a white sublimate Sb_2O_3 at some distance from assay, volatile in OF, coloring flame greenish. The fused bead, on removing the flame, burns forming crystals of oxide; let fall on paper it leaves a black track; fused on Platinum with $Na_2CO_3 + KClO_3$ insoluble metantimonate Na_3SbO_4 forms.

ANTIMONIOUS COMPOUNDS, Sb'''.

Use $SbCl_3 + HCl$ or Tartar emetic, $SbOKC_4H_6O_6$—Potassium antimonyl tartrate.

Water, in excess, pps white basic salt, HCl if not present should be first added, when the pp consists of oxychloride

(SbOCl, etc.), sol in tartaric acid or excess of HCl, which prevent precipitation.

KHO pps Sb_2O_3 from acid solutions; sol in excess as K antimonite.

NH_4HO pps Sb_2O_3 from acid solutions; almost insol in excess.

H_2S pps from acid solutions orange-red Sb_2S_3; insol in dil acids; sol in hot or conc HCl, almost insol in NH_4HO or $(NH_4)_2CO_3$, compare As; sol in KHO and $(NH_4)_2S$ or Na_2S as thio-antimonite, reppd on acidulating; conc HNO_3 oxidizes it, and most compounds, to insoluble Sb_2O_5. Dried and heated in closed tube, a sublimate of Sb_2OS_2 forms near assay, brownish red.

$(NH_4)_2S$ pps Sb_2S_3; sol in excess, reppd by HCl.

ANTIMONIC COMPOUNDS, Sb^V. Use $KSbO_3$ antimonate.

HCl pps Sb_2O_5 from alkaline solutions on careful neutralization.

The behavior of pentad Sb resembles that of triad so closely that the tests need not be repeated; the sulphide Sb_2S_5 is of a somewhat lighter orange color than Sb_2S_3, but both vary with conditions of precipitation.

Tests applicable to all compounds of Sb. Use any salt. Place a piece of platinum in a solution slightly acid with HCl and on it a piece of zinc: A black or brown stain *on platinum* is metallic Sb; slowly soluble in dil HCl. Part of the metal escapes as SbH_3.

Acidulate with HCl, leave copper wire in solution for an hour; blackish gray metal is reduced. Compare Reinsch's test for As.

Formation of Stibine: Follow directions for Marsh's test for As. Sb spots are sooty black; if basin is held a little way from flame a white spot forms, insol in water; the rings of metal formed on heating outlet tube are less volatile than with As.

ARSENIC As''' or ^{V} 75. See also arsenious and arsenic acids.

In closed tube most arsenic compounds yield a sublimate or volatilize. In closed tube mixed with dry Na_2CO_3 and charcoal they give a steel grey mirror of metal. On charcoal in RF all yield a remote white sublimate—very volatile—and a characteristic garlic odor.

ARSENIOUS COMPOUNDS $As.'''$ Use $Na_2HAsO_3 + HCl$ or $As_2O_3 + HCl$, equivalent to solutions of $AsCl_3$.

HCl only precipitates concentrated solutions of alkaline arsenites.

From solutions made acid with HCl:

H_2S pps readily yellow As_2S_3; insol in dilute acids; ***insol in conc HCl***; sol in HNO_3 or aqua regia as As_2O_5; sol in KHO, NH_4HO, $(NH_4)_2S$, $(NH_4)_2CO_3$ as thio-arsenite reprecipitated by acidulating with HCl as As_2S_3.

As_2S_3, dried and heated in closed tube sublimes as orange yellow As_2S_3, darker while hot.

$(NH_4)_2S$ pps As_2S_3, sol in excess or in alkalis, reppd by HCl.

ARSENIC COMPOUNDS As^{V}. Use $Na_2HAsO_4 + HCl$, equivalent to $AsCl_5$.

H_2S gives no pp at first or with neutral solutions; on heating to 70°C it slowly pps yellow As_2S_3, mixed with S (and As_2S_5) pp has the properties of As_2S_3. Precipitation is

more complete if As^{V} be first reduced to As''' by SO_2, and excess of SO_2 boiled off.

$(NH_4)_2S$ pps from acid solutions $As_2S_3 + S$; sol in excess; reppd by HCl as As_2S_5.

Use either of above solutions for following tests, applicable to either As^{III} or As^{V}.

Reinsch's test: Acidulate with HCl, insert a piece of bright copper wire, remove after an hour or two, grey As or Cu_5As_2 is reduced upon it. Dry thoroughly, place in small closed tube and heat, a white crystalline sublimate of As_2O_3 forms; with much, grey As may also sublime. Compare Sb.

Marsh's test: Formation of arsine. Bend a piece of glass tube (about 12 inches long x $\frac{3}{16}$), twice at right angles └——┐, make a moderately fine jet at one end and fit the other by a cork to a medium sized-test tube. * In the latter put 4 or 5 small pieces of zinc (purest obtainable) and nearly half fill with sulphuric acid, diluted about 1:5; when effervescence commences add a few drops of the solution to be tested, adjust cork and *when air is expelled* light gas at jet. Hold a *cold*, *dry* evaporating dish so that its interior is *quite close* to jet; the AsH_3 is decomposed and a black *mirrorlike* spot of As forms. Traces of As in wall-paper, etc., can be found in this way. On heating the straight part of outlet tube a mirrorlike ring of metal forms in it, which is not difficult to volatilize.

NOTE—The sulphides of As, Sn and Sb, if dissolved in alkaline hydrates (NaHO), or in normal colorless (mono) sulphides, (Na_2S), are reprecipitated on neutralization by acids in the same form; but if previously mixed with sulphur or dissolved in the yellow sulphides [containing polysulphide (Na_2S_5)] they are always reprecipitated by acids as the higher sulphides—e. g. SnS is converted into SnS_2, etc.

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* This apparatus should be kept for testing for As, as it serves to detect it in presence of all other metals (compare Sb). Make a blank test to prove whether As is contained in the zinc or acid used, it is rarely absent, but the faint spots thus obtained can be compared with those obtained in the actual analysis.

Colorless alkaline sulphides always contain some polysulphide, being slowly decomposed by light, becoming gradually yellow, hence on acidulating free S is always deposited, white and finely divided. The sulphides used in the laboratory should be only faintly yellow, or the S thus precipitated may mask the precipitate of As_2S_3, etc.

Gold and Platinum fall in analysis with the arsenic group, but are usually tested for specially. All their compounds are readily reduced to metal by heating on charcoal in the oxidizing flame, gold being yellow and fusible, platinum grey and infusible.

GOLD Au^{III}. 197. Use $AuCl_3$.

$SnCl_2$ pps "Purple of Cassius," containing finely divided metal.

$FeSO_4$, SO_2, and reducing agents pp brown metal.

H_2S pps black sulphide, difficultly soluble in alkaline sulphides; sol in KCN or aqua regia.

Filter paper moistened with a gold solution and burned leaves a purplish ash.

PLATINUM Pt^{IV}. 194.8 Use $PtCl_4$.

KCl pps yellow double chloride $2KClPtCl_4$, insoluble in alcohol or ether.

NH_4Cl gives a similar pp.

H_2S pps black sulphide; sol in alkaline sulphides and aqua regia.

SEPARATIONS.

After finishing the reactions of the metals take the prepared solution, No. 1, which contains all the metals of the silver group; precipitate the group, following the directions given in table II, and then separate or distinguish the individual metals as directed in table under Pp I. Refer to the notes made on your previous work with those metals and see that you understand thoroughly the reasons for each step taken.

Treat similarly No. 2, containing all the alkali and alkaline-earth metals, No. 3 containing all the metals of the iron group, and No. 4 containing all the arsenic and copper groups dissolved or suspended. Precipitate each group, and separate its members. Make notes in tabular form.

METALLIC OXIDES AND HYDRATES.

The oxides of the heavy metals are insoluble in water, except As_2O_3 As_2O_5 CrO_3, which act as acids; most of them dissolve in the strong acids, forming salts. The colors of the more commonly occurring oxides are:—White, those of the alkalis and alkaline earths, Al_2O_3, As_2O_3, As_2O_5; white to yellowish, ZnO, CdO, Sb_2O_3, Sb_2O_4, Sb_2O_5, Bi_2O_3, SnO_2; brown to black, CuO, Hg_2O, Fe_3O_4, Ni_2O_3, CoO, PbO_2, MnO_2, Mn_3O_4, Bi_2O_2; brown, Ag_2O; yellowish, PbO; yellow to red, HgO; red brown, Cu_2O, Fe_2O_3; red, Pb_3O_4; green, Cr_2O_3, NiO.

Hydroxides of the heavy metals are insoluble in water, those of the alkalis and alkaline earths are soluble (Mg slightly) and turn litmus blue. With acids they form salts and water. Dilute acids, as HCl, dissolve them all, those of Al, Cr, Fe and Sn with difficulty, forming salts.

Heated in closed tube all hydrates, except those of Ba and the alkalis, give off water. Other substances containing water, combined or mechanically enclosed, also give it off when heated.

EFFECTS ON METALS OF HEAT AND THE ORDINARY SOLVENTS.

Use very small quantities of metal, not over $\frac{1}{20}$ gram or one grain for each test; rarer ones may be omitted. Treat in test tube with 4 or 5 ccs of moderately dilute acid (1 concentrated acid to 3 water) raising temperature gradually.

	Color, etc.	Heated on Charcoal, O F.	Moderately dilute HCl	Moderately dilute HNO_3	Dil. H_2SO_4	Conc. H_2SO_4	Aqua Regia	KHO
K, Na	White, soft	Oxidized	Oxidized	by water and	dissolved as	hydrate		
Mg	White, mall.	Burns	Sol.	Sol.	Sol.			
Zn	White mall. if not	Fus. Ox. (burns) sub.	Sol.	Sol.	Sol.			Sol.
Cd	White crystalline	Fus. vol. sub.	Sol	Sol.	Slowly sol.			Insol.
Al	White, mall.	Fus. ox.	Sol.	almost	insoluble			Sol.
Fe	Grey, magnetic	Infus ox.	Sol. Fe''	Sol. cold Fe'' hot Fe^{IV}*	Sol. Fe''	Ins. cold, sol. hot Fe^{IV} ev. SO_2	Sol.	Ins.
Ni	White, magnetic	Infus.	Sol.	Sol.*	Sol.	Insol. Cold Sol. Hot Evolving SO_2	Sol.	Ins.
Cu	Red, mall.	Diff. fus.	Insol. †	Sol.	Insol.		Sol.	Ins.
Ag	White, mall	Diff fus.		Sol.*			Surface attacked	Ins.
Hg	White, liquid	Vol.		Sol. cold or dil. Hg' conc. Hg''			Sol. $HgCl_2$	Ins.
Bi	Red-grey, brittle	Fus sub.	Insol.†	Sol.			Sol.	Insol.
Sb	Grey, brittle	Fus. ox. sub.	Slowly sol.	Ox. insol.			Ox. slightly sol.	Insol.
As	Grey, brittle	Vol. sub. garlic odor	Insol.	Ox. sol. As_2O_5			Sol. As_2O_5	Sol.
Sn	White, mall.	Fus. ox. (sub)	Sol. Sn''	Oxidized insol. $SnO(HO)_2$	Slowly sol.	Sol.	Sol. $SnCl_4$	Sol. hot
Pb	Bluish, soft, mall.	Fus. ox. sub.	Insol.	Sol	Insol.	Ins. surf. attacked	Surf. attacked	
Pt	White	Infus.	Insoluble				Sol. $PtCl_4$	
Au	Yellow	Diff. fus.					Sol. $AuCl_3$	
S	Yellow, brittle	Fus. burns, SO_2	Ins.	Ox. SO_3	Ins.	Ox. SO_2	SO_3	Sol. $K_2S_5+K_2S_2O_3$
C	Black	Inf. burns slowly	Ins.	Ox. CO_2		Ox. CO_2+SO_2		Insol.

*Conc. HNO_3 renders these metals "passive" and insoluble even in dilute acid. †Presence of air enables HCl to slowly dissolve Cu, Bi, etc.

Generally speaking the more + metals are most readily attacked by acids, the impure much more readily than pure, and imperfectly mixed alloys more than homogeneous; contact with a less + metal (Pt) sets up galvanic action and hastens solution

Heating, fine division and roughness of surface facilitate action, rapidity of solution varying with surface exposed. Moderately strong acids are usually most active. Solution may be retarded or prevented by over-concentration or over-dilution of solvent, by liquid becoming saturated with salts produced or by their insolubility in the acid used, especially if concentrated, thus forming a protective coating over the metal. A mere film of grease (or oxide e. g. Fe_3O_4) may quite prevent action.

Fus., fusible; inf., infusible; ins., insoluble; mall., malleable; ox., oxidized; sub., sublimate; vol., volatile.

BEHAVIOR OF THE COMMONER GASES AND NON-METALLIC ELEMENTS.

Take small quantities and test; make the tests with which you are not familiar; the gases can be prepared in small test-tubes by the methods indicated.

Phosphorus P. On heating burns readily, forming P_2O_5. Yellow variety inflammable on rubbing, has characteristic odor, soluble in CS_2; red possesses opposite properties. Any solid compound of P (use $Ca_3P_2O_8$) heated in closed tube with Mg, forms Mg_3P_2, and on moistening gives off PH_3 with garlic odor.

Sulphur S. On heating, fuses and burns with odor of SO_2. Ordinary varieties yellow; insoluble in acids; sol in CS_2 and KHO. Oxidized by Br, Cl or HNO_3 to H_2SO_4. With $KClO_3$ or KNO_3 deflagrates on heating. The precipitated variety is finely divided and passes through filter paper.

All S compounds (use any sulphate) fused with Na_2CO_3 on charcoal, in RF form Na_2S. Placed on silver and moistened this gives a black stain.

Carbon C. Ordinary varieties black. Burns slowly to CO_2 on heating; with $KClO_3$ or KNO_3 deflagrates on heating.

Iodine I. Blackish crystals. In closed tube violet irritating vapor, and crystalline sublimate. Sol in CS_2 or Kerosene, coloring them, traces turn starch blue; colors removed by Cl or KHO.

Bromine Br. (Heat conc H_2SO_4, KBr and MnO_2). Red irritating vapor, condensing to dark heavy liquid, bleaches litmus. Soluble in water (reddish) and CS_2. With KI and starch gives blue color, due to free I.

Chlorine Cl. (Warm MnO_2 with conc HCl). Yellowish gas, suffocating smell, bleaches litmus or indigo instantly.

Soluble in water, yellowish. Shaken with KI and starch traces liberate I giving blue color. Oxidizes more strongly than Br or I.

Oxygen O. (Heat HgO or $KClO_3$ in small tube). Colorless odorless gas; re-ignites glowing splinter. Red fumes if mixed with NO.

Nitrous Oxide, N_2O. (Heat NH_4NO_3). Colorless gas; re-ignites glowing splinter; not affected by mixing with NO or O.

Nitric Oxide NO. (Heat Cu and conc HNO_3). Colorless gas, with air or O forms red acid fumes of NO_2. Shaken with $FeSO_4$ gives black $(FeSO_4)_2NO$.

Nitrogen Tetroxide NO_2. Red fumes, soluble in water, reddening litmus; formed by NO and air or O.

Nitrogen N. (Heat $K_2Cr_2O_7 + 2NH_4Cl$). Does not burn or support combustion. Chemically inactive.

Hydrogen H. (From Zn + dil H_2SO_4). Colorless odorless gas, lighter than air; burns in air, mixed with air is explosive.

Carbon dioxide CO_2 (Na_2CO_3 + dilute H_2SO_4). Colorless gas, heavier than air, extinguishes glowing splinter; drop of $Ba(HO)_2$ solution held in it becomes milky.

Carbon monoxide CO. (Oxalic acid with conc H_2SO_4). Burns with blue flame.

Sulphur dioxide SO_2. (Cu + conc H_2SO_4). Characteristic odor; sol water, reddens and then bleaches blue litmus. Reduces ferric salts to ferrous.

Hydrogen sulphide H_2S. (FeS + dil H_2SO_4). Characteristic odor; soluble in water; blackens paper moistened with lead salt. Burns in air with odor of SO_2; oxidizing agents pp S. Reduces Ferric salts to ferrous. H_2S and SO_2 decompose each other.

Ammonia NH_3. ($NH_4Cl + KHO$). Characteristic odor; very soluble in water, blues litmus, white fumes with HCl gas.

Hydrochloric acid HCl. ($NaCl + H_2SO_4$). Pungent acid fumes, very soluble in water; redden litmus; with MnO_2 gives off Cl.

REACTIONS OF THE ACIDS.

SULPHIDES. (See reactions of Sulphur).

Hydrosulphuric acid, H_2S. Use FeS_2, ZnS and $(NH_4)_2S$.

Sulphides of heavy metals are insoluble in water (Al and Cr decomposed), those of the alkalis and alkaline earths are soluble, and their solutions blacken silver foil or lead paper. Most are strongly colored.

With *HCl* the soluble sulphides and many others evolve H_2S, effervescing on warming; recognized by its odor and action on paper moistened with a drop of lead acetate, forming PbS.

Heated on charcoal in OF all are oxidized, giving the odor of SO_2.

SULPHATES. (See reactions of Sulphur.)

Sulphuric acid H_2SO_4, anhydride SO_3. Use Na_2SO_4.

Most sulphates are soluble in water, those of Pb Ba Sr insoluble; $CaSO_4$ is slightly soluble, soluble in HCl; all are insoluble in alcohol, and the slightly soluble ones are precipitated on adding it.

Heated in closed tube, or on charcoal, sulphates of the heavy metals and Mg give off SO_2 (mixed with SO_3).

$BaCl_2$ or $Ba(NO_3)_2$ pps white $BaSO_4$ from solutions; insol in dil HCl, even on boiling.

$Pb(C_2H_3O_2)_2$ pps white $PbSO_4$; sol in HNO_3 or KHO. $BaSO_4$ is little affected by boiling with Na_2CO_3, $PbSO_4$ forms $PbCO_3$.

Free sulphuric acid gives white fumes on evaporating to near dryness; at this stage it blackens sugar or paper.

NITRATES.

Nitric acid HNO_3, anhydride N_2O_5. Use KNO_3.

All are soluble in water, except a few basic nitrates (Hg Bi Fe^{IV}).

Heated on charcoal all deflagrate.

In closed tube all give off O on strong heating; those of heavy metals also give red fumes ($NO_2 + O$) leaving oxides.

Conc H_2SO_4 decomposes all nitrates liberating HNO_3, on adding metallic copper this is reduced forming red fumes.

$FeSO_4$ reduces HNO_3 to NO (forming ferric sulphates) and with it forms black $(FeSO_4)_2NO$. To apply as a test:—treat the nitrate, solid or solution, in a test tube with conc H_2SO_4, warm gently, allow to become quite cool and pour on it an equal bulk of $FeSO_4$ solution. This floats on the heavier liquid, and at their juncture a dark ring is seen, becoming more apparent if the tube is gently rocked; heating destroys the color. (NB. Nitrites give this reaction and also deflagrate on charcoal.)

Free nitric acid with metallic Cu gives off NO, forming red fumes of NO_2 in air.

CHLORIDES.

Hydrochloric acid HCl. Use NaCl.

All dissolve in water except AgCl and Hg_2Cl_2; $PbCl_2$ is soluble in hot and slightly in cold water. Cu_2Cl_2 is slightly soluble.

Solid chlorides heated in $NaPO_3$ bead with CuO, color flame green ($CuCl_2$).

Conc H_2SO_4 (or $HKSO_4$ with solids) gives off pungent fumes of HCl. On adding MnO_2 chlorine is formed, recognized by odor, color and bleaching properties.

$AgNO_3$ after slightly acidulating with HNO_3 pps white curdy AgCl, turning purple in sunlight; sol NH_4HO, reppd by HNO_3; sol KCN, $Na_2S_2O_3$ and to some extent in other chlorides; almost insol in HNO_3.

Free HCl evolves Cl with MnO_2.

Chlorides, heated with excess of HNO_3, form nitrates; and nitrates heated with HCl form chlorides; in each case Cl and NOCl are liberated.

CARBONATES.

Carbonic anhydride CO_2. Use Na_2CO_3 and $CaCO_3$.

Carbonates of the alkalis dissolve in water, a few dyad bicarbonates are soluble, but precipitate on boiling; the reactions are alkaline, those of bicarbonates neutral.

HCl produces an effervescence with all carbonates, some requiring heat. CO_2 escapes, recognized by producing turbidity in a drop of $Ba(HO)_2$.

Effervescence without odor on addition of an acid indicates a carbonate.

In solution $BaCl_2$ pps white $BaCO_3$, sol in acetic acid or HCl with effervescence.

PHOSPHATES. (See reactions of Phosphorus.)

Ortho-phosphoric acid H_3PO_4, anhydride P_2O_5. Use Na_2HPO_4.

Only the alkaline salts dissolve in water, all dissolve in HCl or HNO_3.

Neutral solutions treated with NH_4Cl, NH_4HO *and* $MgCl_2$ pp white $MgNH_4PO_4$; insol in NH_4HO; sol in acids.

$HNO_3 + (NH_4)_2MoO_4$ (ammonic molybdate) pps yellow ammonium phospho-molybdate on standing; soluble in NH_4HO.

N. B. Arsenic and silicic acid must be removed before testing for P_2O_5.

SILICATES.

Silicic acid H_2SiO_3, H_4SiO_4, anhydride SiO_2. Use water-glass Na_2SiO_3, and clay (hydrated silicate of aluminium and iron).

Silicates of the alkalis dissolve in water; these are decomposed by acids forming soluble silica, on evaporating or boiling, gelatinous $Si(HO)_4$ is deposited. Many others are unaffected by acids, others are partly or wholly decomposed and on evaporation leave gelatinous $Si(HO)_4$; on heating this SiO_2 is formed, insoluble in acids.

SiO_2 and silicates insol in acids are insoluble in a bead of microcosmic salt, floating about as a "skeleton."

SiO_2 and insoluble silicates, fused on Platinum with 4 or 5 parts of Na_2CO_3 or $NaKCO_3$, form alkaline silicates, which dissolve in hot water, leaving metallic oxides or carbonates insoluble; on acidulating with HCl or HNO_3 evaporating to dryness and treating with hot dilute HCl, SiO_2 remains insoluble.

Precipitated or gelatinous silica dissolves in KHO or Na_2CO_3, not in acids.

BORATES.

Boric acid H_3BO_3. Use $Na_2B_4O_7$.

Those of the alkalis are soluble, others insoluble or nearly so.

Conc H_2SO_4 liberates H_3BO_3, from strong solutions this crystallizes out; stirred with alcohol the H_3BO_3 dissolves and on burning it the flame is tinged green.

Solids moistened with conc H_2SO_4 and held on platinum wire at base of flame color it bright green.

FLUORIDES. Hydrofluoric acid HF. Use CaF_2.

All fluorides are insoluble except those of Hg″Ag and the alkalis.

Conc HCl dissolves most of them, (CaF_2 but slightly, it is reppd by ammonia, white. CaF_2 is completely decomposed by H_2SO_4).

Conc H_2SO_4 decomposes fluorides evolving HF, pungent fumes resembling those of HCl; *etching glass.* A support of platinum, iron or lead should be used; presence of B or Si (of glass) prevents reaction, forming volatile BF_3 or SiF_4.

BROMIDES. Hydrobromic acid HBr. Use KBr.

In solubilities they resemble chlorides.

Conc H_2SO_4 gives HBr + Br, with MnO_2 free Br is evolved as brown irritating fumes, bleaching litmus; on diluting, adding a little CS_2 and shaking the latter becomes red from dissolved Br; color not removed by Cl water.

Cl water liberates Br.

$AgNO_3$ pps yellowish white AgBr, difficultly sol in NH_4HO, otherwise like AgCl.

IODIDES. Hydriodic acid HI. Use KI.

Iodides resemble chlorides in solubility.

Conc H_2SO_4 gives off HI and I, with MnO_2 free I is evolved as violet vapor condensing to black crystals. On diluting and shaking with CS_2 the latter becomes violet from dissolved I, color removed by sufficient Cl.

Cl water liberates I and in excess combines with it.

Potassium nitrite with acetic acid.liberates I.

$AgNO_3$ pps yellowish AgI; almost insol in NH_4HO; sol KCN.

$Pb(C_2H_3O_2)_2$ pps yellow PbI_2; sol in excess, in hot wate and in KHO.

CYANIDES. Hydrocyanic acid HCN or HCy. Use KCN.

Cyanides of the alkalis and alkaline earths are soluble and react alkaline; others are insoluble (except Hg″), but many dissolve in KCN as double cyanides. They are strong reducing agents. KCN heated on charcoal with oxides or sulphides of heavy metals reduces them to the metallic state, forming KCNO or KCNS (cyanate or thio-cyanate). The acid and most of its soluble salts are highly poisonous.

HCl and most acids decompose most cyanides, evolving HCN with characteristic odor of almonds, *highly poisonous.*

$AgNO_3$ after acidulating with HNO_3 pps white AgCN; sol in NH_4HO; decomposed by boiling with HNO_3, otherwise like AgCl.

$FeSO_4$ does not give a blue color at first, but on making alkaline with KHO, shaking well and acidulating with HCl, a pp of Prussian blue forms.

DOUBLE CYANIDES are of two classes, those which give off HCN with very dilute HCl and those not readily decomposed by dilute HCl; the most important of the latter are the Ferro and Ferri-cyanides.

The salts of the alkalis and alkaline earths alone are soluble, very dilute HCl does not affect them readily; concentrated or hot acids evolve HCN. Heated on charcoal they evolve N and leave magnetic residues.

	FERRO-CYANIDES. Use K_4FeCy_6	FERRI-CYANIDES. Use $K_6Fe_2Cy_{12}$
Solution colored.......	yellowish	orange red
$FeSO_4$ pps...........	light blue	Turnbull's blue
Fe_2Cl_6 pps...........	Prussian blue	no pp
$CuSO_4$ pps............	brown	greenish

THIOCYANATES or Sulphocyanides.

Thiocyanic acid $HCNS$. Use $KCNS$.

Fe_2Cl_6, after acidulating, gives blood-red color $Fe_2(CNS)_6$, removed by HCl.

HCl, H_2SO_4 gradually evolve HCN.

SULPHITES. Sulphurous anhydride SO_2. Use Na_2SO_3.

Sulphites of the alkalis alone are soluble in water, all are decomposed by acids. Cl or Br oxidizes them to sulphates.

HCl evolves SO_2 recognized by odor.

$BaCl_2$ pps white $BaSO_3$; sol in HCl.

THIOSULPHATES (or Hyposulphites). Use $Na_2S_2O_3$.

All thiosulphates are more or less soluble, those of alkalis readily. Sodium hyposulphite forms a double salt with silver.

HCl evolves SO_2 and pps *yellow* sulphur.

$BaCl_2$ pps white BaS_2O_3; sol in HCl leaving a residue of S.

Salts of the Thionic acids ($H_2S_2O_6$, $H_2S_5O_6$, etc.) and true hyposulphites (H_2SO_2) are not often met with; like all other substances containing S they give the "Sulphur reaction" with silver, after reduction with sodium carbonate.

CHLORATES, $HClO_3$. Use $KClO_3$.

All are soluble. Heated on Charcoal they deflagrate violently.

In closed tube all evolve O on heating and residue is found to contain chloride.

Conc H_2SO_4 yields oxides of Cl, dangerously explosive.

Conc HCl evolves oxides of Cl with characteristic chlorous odor.

Bromates and Iodates deflagrate on charcoal, in closed tube they evolve oxygen and yield bromides or iodides.

ACETATES.

Acetic acid. H $C_2H_3O_2$. Use ammonium acetate.

All are soluble in water.

With H_2SO_4 acetic acid is liberated recognized by odor, on adding a little alcohol fragrant ethyl acetate is formed.

OXALATES.

Oxalic acid. $H_2C_2O_4$. Use ammonium oxalate.

Conc H_2SO_4 evolves CO_2 and CO, the latter burning with blue flame.

$CaCl_2$ pps white CaC_2O_4 insol in acetic acid, sol HCl.

CHROMATES AND DICHROMATES.

Chromic acid H_2CrO_4, dichromic $H_2Cr_2O_7$, anhydride CrO_3. Use $K_2Cr_2O_7$.

Solutions have yellow color.

Reducing agents in presence of free acid form chromic salts; thus; $H_2S + HCl$ forms green Cr_2Cl_6 and pps S.

$BaCl_2$ pps yellow $BaCrO_4$ insol in acetic acid, sol HCl.

$Pb(NO_3)_2$ pps yellow chromate, sol in KHO.

ARSENITES AND ARSENATES,

Arsenious acid H_3AsO_3, arsenic H_3AsO_4; anhydrides As_2O_3, As_2O_5. Alkaline salts are soluble, use a solution of the sodium salts.

Reactions in Solution.

		ARSENITES.	ARSENATES.	
$AgNO_3$	pps	yellow Ag_3AsO_3,	red-brown Ag_3AsO_4	Sol NH_4HO, HNO_3 and ammonic salts, must be carefully neutralized before test.
$CuSO_4$	"	green $CuHAsO_3$,	blue-green $CuHAsO_4$	
$HCl + H_2S$	"	yellow As_2S_3 readily	yellow $As_2S_3 + S$ on heating or standing.	

Arsenites are oxidized to arsenates by HNO_3, etc.

Arsenates act like phosphates with Mg and MoO_3, hence must be removed by H_2S before testing for P_2O_5.

ANALYSIS OF UNKNOWN SUBSTANCES.

Determine the composition of the substances submitted to you. A preliminary blow-pipe examination should be made and followed by a wet analysis. The tables given are intended as a guide for the latter, but should not be blindly followed, and on no account used until the reactions of the individual metals and acids have been studied.

The first twelve substances are *simple*, containing not more than one acid and one base, without reckoning water or traces of impurities. If the student makes a practice of noting closely the appearance, crystalline form, color, etc., of all the chemical compounds he meets with, a glance will often indicate what the probable composition of an unknown salt may be. The analysis of a simple salt is comparatively easy, the groups in which the metal falls is first determined, the color of group precipitate serves as a guide for the special tests then to be applied: the acids should next be tested for, beginning with the common ones. The mixtures and complex solutions may contain any bases or acids.

Most of the substances present are indicated in the blowpipe examination. In the wet analysis the principal danger lies in taking too much or too little of the substance to work with, especially the former; this entails heavy precipitates, bulky solutions, slow filtration and loss of time. Nearly all the work can be done in testtubes, using small beakers and flasks if necessary. Great care must be taken to insure the exclusion of foreign matters, covering beakers, etc, if left for any length of time.

Several operations may, with due care, be carried on at one time thus the silver and copper group and acids can be tested for while the remainder of the group precipitation is going on.

Brief notes should be made, preferably in tabular form, and and all the observations and treatment indicated. If left over night label all precipitates and solutions distinctly, or confusion will occur. Unless a test is perfectly conclusive confirm it by another. In returning results note which substances are present in considerable quantity and which in traces only.

In connection with tables consult notes at end of book.

TREATMENT OF UNKNOWN SUBSTANCES.

Not metals or alloys.

A LIQUIDS. Go on at once to test for metals, afterwards for acids (see tables and page 56).

B SOLIDS, Note closely appearance and general physical properties. Test small portions in dry way (see page 54). Treat a very small quantity of powder in test tube with 10ccs water, boil for some minutes.

I. *Completely Soluble*, dissolve ½ to 1 gram in water and proceed as in A.

II. *Not entirely soluble.* Boil ½ to 1 gram of fine powder in distilled water for five minutes, pour or decant off clear liquid; if it does not appear to dissolve at all evaporate a few drops of liquid to dryness on watchglass or platinum foil, note if a residue remains. Treat insoluble portion with dilute HCl, if soluble on boiling proceed as in A.

(Note. In most cases time can be saved by using HCl on the solid at the outset.)

If that fails use a little conc$^{\underline{d}}$ HCl, and if still insoluble use a little HNO_3 or Aqua regia.

The use of HNO_3, Aqua Regia or excess of HCl is to be avoided if possible. Nearly all substances dissolve in HCl; a few sulphides etc., require to be oxidized by HNO_3. The portions soluble in water and acids respectively may be mixed or tested separately for bases (see notes), a precipitate may fall on mixing them.

III. Portion insoluble in water and acids. (See page 58.)

PRELIMINARY EXAMINATION.

COLOR etc. Compounds of NH_4, Na, K, Ba, Sr, Ca, Mg, Zn, Al are white or colorless unless combined with coloring acids as are most compounds of As, Sb, Sn, Cd, and many of Hg, Pb, Bi, Ag. Most sulphides, and the oxides and iodides of heavy metals are strongly colored. Most salts of Cu, Cr, Fe, Mn, Ni, Co have characteristic colors.

Soluble in water. All salts of alkalis, nearly all nitrates, sulphates, chlorides, bromides, iodides, chlorates, acetates, nitrates, thiosulphates.

Insoluble in water. Most carbonates, phosphates, silicates, sulphites, fluorides and oxalates (of alkalis excepted) oxides, hydrates and sulphides of heavy metals and Mg; Sulphates of Ba, Sr, Ca, Pb, chlorides, bromides and iodides of Ag, Hg^I, (Cu^I) and Pb. A few oxychlorides, basic nitrates, and basic salts generally. Most minerals.

Heat a small portion in closed tube.

No change occurs on strong ignition	Absence of water, volatile or fusible substances
Infusible white residue.	SiO_2 Al_2O_3 etc.
Changes color	White or yellow, darker hot Zn Sn Pb Bi Red, darker hot Fe_2O_3 HgO Blackness permanently, odor of burning Organic matter
Gives off water	Water of crystallization, constitution, hygroscopic or mechanically enclosed
Gives off gas (Test with litmus and glowing splinter)	Supports combustion, O or N_2O from peroxides chlorates nitrates nitrites Red fumes, odor of NO_2 } reddening litmus — Nitrates, nitrites } of heavy metals Odor of SO_2 — Sulphates Sulphites CO_2, pps $Ba(HO)_2$ — Some carbonates & oxalates CO, burns with blue flame Oxalates, organic matter Odor of H_2S Some sulphides. Odor of NH_3, blues litmus Ammonia compounds
Sublimate forms	Yellow to orange S, As_2S_3 HgI_2 Reddish (black hot) Sb_2S_3, Black HgS Mirror, silvery Hg, steelgrey As, White, salts of As, NH_4, Hg and some of Sb.

Confirm these by heating with dry Na_2CO_3 and charcoal in closed tube. Mirrors of As or Hg, odor of NH_3.

Heat on charcoal in oxidizing flame of blowpipe.

Decrepitates	Alkaline chlorides, many crystals and minerals
Deflagrates	Nitrates, chlorates, etc
Odor of SO_2	Sulphides, sulphates, etc
Powder readily blown away by blast	Due to escape of gas, usually water or CO_2
Fuses	Chlorides, salts of alkalis, etc., not very characteristic.
Fuses, gives up water and re-solidifies	Water of crystallization
Fuses and sinks	Salts of alkalis
Sublimate forms	White remote volatile As (Hg, NH_4, $PbCl_2$) nearer Sb.
	Near assay, yellowish cold, yellow to brown hot, volatile Pb Bi
	Very near assay, white cold, yellow hot
	Non volatile Zn (Sn)
White infusible residue.	Ba Sr Ca Mg Al SiO_2
Colored residue	Many heavy metals, magnetic Fe

Mix with Na_2CO_3, heat on charcoal in reducing flame.

Sublimates	As Sb Pb Bi Zn Sn as above.
Odor of garlic	As
Reduced to beads of metal.	Brittle, fusible, Sb, Bi; malleable bluish fus Pb
	White fus. Sn; less fus. Ag
	Red, difficult to fuse Cu

Dig out residue and coal that has absorbed flux, powder and test with magnet, magnetic Fe Ni Co. *Lay powder on silver coin, add a drop of water,* black stain indicates a compound of *sulphur.*

Test a small portion of powder in borax bead, O F then in R F

[Substances containing S, As or easily reducible metals ~~should~~ first should first be thoroughly roasted on charcoal in OF, and non-volatile residue treated.]

Bead is colored blue *Co*, green *Cr*.

Green hot, bluish cold, OF, red and opake when cold RF, *Cu.*

Brown (violet hot) OF turbid RF, *Ni.*

Violet OF, colorless RF *Mn.*

Yellow to red hot, lighter cold OF, greenish RF *Fe.*

Yellowish hot colorless cold OF, turbid in RF, Sb Pb Bi Zn etc.

EXAMINATION IN WET WAY.

Test first for metals and bases.

I. If originally liquid evaporate 1 cc to dryness on watch-glass over waterbath, note amount and appearance of residue and test for flame coloration.

II. If liquid or soluble (wholly or partially) in water test liquid or aqueous solution with litmus.

Acid reaction indicates free acid, acid salts, or salts of strong acids with heavy metals.

Alkaline reaction indicates alkaline or alkaline earthy hydrates, sulphides, or cyanides, or carbonates of alkalis, and salts of weak acids generally.

Neutral reaction is seen in comparatively few salts.

III. Test a small portion of *original substance* for *ammonia* by heating with KHO.

Test a few drops for *iron* by K_4FeCy_6, a heavy blue pp falls if much is present, traces give blue solution. If strongly acid neutralize first and add acetic acid before testing.

If iron is present determine whether ferrous or ferric by $K_6Fe_2Cy_{12}$ and KCNS, before solution can oxidize.

IV. Test a considerable portion of solution for metals (Table II.) afterwards test solution or original substance for acids; it is of course useless to test for any acid in a solution prepared with its aid.

TESTING FOR ACIDS.

Having determined the metals present a little consideration will often show what acids are likely to be present and some which are excluded, e. g. if Ba is found in a substance which dissolves in HCl no sulphate is present. Several acids also will have been found while testing for metals—carbonic, silicic phosphoric. If arsenious, arsenic or chromic acid is present As or Cr will have been precipitated.

Take successive small portions of original substance for the following tests:

I. Add dil HCl and heat:

Effervescence without odor indicates a *carbonate*, test for CO_2

Odor of H_2S, blackening lead paper, shows *sulphide.*

Odor of SO_2, *sulphite* or *thiosulphate*, the latter deposits S.

Odor of almonds (HCN) shows a cyanide.

Red fumes NO_2 show a *nitrite*, NOCl on heating, a *nitrate.*

To the HCl solution add $BaCl_2$ white pp, insol in acids indicates a *sulphate.*

In presence of silver group use $HNO_3 + Ba(NO_3)_2$ for latter test.

II. Add dil HNO_3 in some excess and warm gently, add $Ag\ NO_3$:

White pp, insol in HNO_3. soluble after washing in NH_4HO, shows a *chloride.*

White pp sol in NH_4HO, decomposed by boiling HNO_3 a *cyanide.*

Yellowish pp insol in HNO_3, slightly sol in NH_4HO *Bromide.*

Yellow insol in $NH_4\ HO$ an *iodide.*

III. Treat with conc $H_2\ SO_4$, warm very gently:

CO_2, H_2S, HCN etc., as above.

Strong acid fumes, HCl or HF from *chlorides* or *fluorides*, confirm HF.

Odor of acetic acid from *acetates.*

Red or brown fumes, odor of NO_2 or NOCl from *nitra*[illegible] *nitrites.*

Brown fumes with odor of Br from *Bromides*, purple I from *Iodides*.

Cool a portion of this, pour on it a solution of $FeSO_4$, *brown ring* from *nitrites* or *nitrates*.

To another portion of this in a basin add alcohol, stir well and set on fire, green flame shows a *borate*.

(Remove copper before testing.)

IV. Test specially with Fe_2Cl_6 and $FeSO_4$ for *thiocyanates* and *ferro* and *ferri-cyanides*; with $CaCl_2$ for oxalates: by etching glass for fluorides, and for arsenites, arsenates, chromates etc., if suspected.

Traces of HCl and H_2SO_4 will be found as impurities in many substances and in reagents. No attempt need generally be made to associate the acids and bases found in a mixture with one another.

For systematic grouping and separation of acids in mixtures see Prescott and Johnson, or Valentin.

PORTION INSOLUBLE IN WATER AND ACIDS.

This can only obtain a limited number of substances viz:

C or S recognized by color or combustibility.

AgCl, soluble in NH_4HO or KCN, $PbSO_4$ sol in KHO or ammonium acetate. Cr_2O_3 green, Fe oxides red or brown, and Al_2O_3, Sb_2O_4, $BaSO_4$, $SrSO_4$ (CaF_2 or $CaSO_4$ only partially dissolved) SiO_2, SnO_2, all white, and some native silicates and aluminates.

Sulphur and *carbon* should be burned off on a piece of porcelain.

A portion of residue should be tested for *Pb and Ag* by the blowpipe fusing with soda on charcoal in RF. The finding of Pb indicates *sulphate* and of Ag *chloride* but the Cl may have been derived from reagents used. If lead [illegible] digest with ammonic acetate and filter, filtrate contains Pb. If Ag digest with NH_4HO and filter.

Cr and Fe are indicated by color.

Heat a portion on charcoal in RF for two or three minutes, moisten with HCl and test in flame, green color shows Ba, crimson Sr, both combined with $H_2 SO_4$, orange red Ca.

SiO_2 is usually gritty and scratches glass if rubbed on it.

Fuse a portion (freed from C, S, Ag, Pb) mixed with 4 parts Na_2CO_3 or $NaKCO_3$ and a little KNO_3 or platinum foil. Boil with water 2 or 3 minutes and filter. Solution may contain, with sodium carbonate, the Cr (as chromate) HF, H_2SO_4, Al, Sb, Sn, SiO_2, test for them.

The residue may contain Al, Fe, Ba, Sr, Ca, Dissolve in HCl and test for these metals.

Usually the amount of insoluble residue is small and will be found only to contain one or two of these substances, readily detected by the blowpipe and flame tests.

TREATMENT OF METALS AND ALLOYS.

Note color and whether malleable, brittle, magnetic or readily fusible. Metals present in any considerable proportion can be detected by the blowpipe. If brittle powder about a a gram, if malleable roll or hammer out thin and cut up into small pieces.

Treat a small portion, about ¼ gram, with 10 or 15 ccs of moderately strong HCl and a like amount with moderately strong HNO_3; keep almost at boiling point for some time. Most alloys are attacked by one or other.

A. If HCl dissolves it readily Bi Sb Pb Hg Ag Cu are not present in large proportion, proceed to test for metals in solution.

B. If HNO_3 *dissolves it readily and completely* Al Cr Sn Sb are not present in large quantity, evaporate down with HCl.

dilute and test for metals (and for P_2O_5 and H_2SO_4 indicating P and S).

C. If HNO_3 *forms a white deposit* insoluble in hot water or dilute HNO_3 Sn or Sb is present; filter wash pp. Treat filtrate as in B; digest pp with yellow $(NH_4)_2S$ and test for Sn and Sb.

N. B. The chlorides and nitrates are less soluble in acids then in water and may fall out as a white deposit, but dissolve in hot water or dilute HNO_3. A slight residue, insoluble in HCl or HNO_3 may be C, Si, Au, Pt.

If the white pp is very heavy dissolve a fresh portion in aqua regia and test as in B.

D. If insoluble in either acid treat with aqua regia, treat as in B and test specially for Au and Pt in concentrated solution. Some alloys of Au + Ag are insoluble in this, they must be alloyed with more Ag or Cu, this removed by HNO_3 and residue attacked by aqua regia.

NOTES

ON GENERAL SEPARATION OF METAL INTO GROUPS.

1. From *too concentrated* a solution many salts may be precipitated on addition of HCl being less soluble in acid than in water.

   On adding water a white pp may form (basic or) oxychlorides of Bi Sb Sn or basic nitrates of Bi or Hg, such pps will generally redissolve on the addition of HCl (§I) or may be decanted off and then either tested separately or treated with a little conc. HCl and added to main solution.

2. Effervescence on addition of HCl, without odor indicates carbonates, with odor of SO_2 sulphites, of H_2S sulphides. If HCl were used to effect solution of the solid none need be added here, but if solid dissolved partly in water and partly in HCl a precipitate may form on mixing the two this may be a member of the silver group, or a carbonate sulphate, etc. In such cases add more HCl till distinctly acid, if pp does not dissolve on warming it is probably a member of the silver group or a sulphate of Ba Sr or Pb.

   Alkaline solutions on being *neutralized* with HCl may precipitate various hydrates, most of which dissolve readily on adding more acid; sulphides of As Sb and Sn, which dissolve with some difficulty (As_2S_3 is insoluble) in HCl and are strongly colored; and various cyanides. The precipitation of sulphides is accompanied generally by evolution of H_2S (or sometimes of CO_2 and HCN), that of cyanides by odor of HCN.

   If a large amount of HNO_3, or aqua regia has been used, or any strong oxidizing agent is present [chlorates, nitrates chromates[*] permanganates, SO_2, Cl, Br or I] indicated by odor of Cl, NOCl, or SO_2, it is best to boil down, add some strong HCl, evaporate to complete dryness and redissolve in dilute HCl.

---

[*] Chromates are indicated by yellow solutions (confirm by neutralizing with NH_4HO and adding $HC_2H_3O_2$ and Pb $(C_2H_3O_2)_2$) permanganates by purple color.

3. The H_2S water should be clear and smell strongly of the gas.

When it is added the solution should be acid but not too strongly acid.

If neutral Fe Ni Co, etc., will be thrown down, if alkaline As Sb Sn may fail to precipitate.

If much free acid is present Cd may fail to pp, and Pb if a great excess of HCl be present, both causing confusion by being precipitated later on in other groups.

From strongly acid solutions Pb may fall at first as brick-red Pb_2SCl_2 becoming black on dilution and addition of more H_2S.

Any large amount of free acid should be gotten rid of by evaporation or partially neutralized with NH_4HO, and diluted.

It must be remembered that *H_2S* in precipitating sulphides *sets acid free*, see note 4.

Milky white S, so finely divided as to pass through a filter, is ppd by the action of H_2S on Fe_2Cl_6, CrO_3, MnO_3, etc., reducing them to $FeCl_2$, Cr_2Cl_6, $MnCl_2$; also from HNO_3 and other oxidizing agents.

Arsenic if present as pentad may be missed if solution is not heated to 70° and an excess of H_2S added. If As^{V} be suspected it can be reduced to As^{III} by SO_2 water and boiling off the excess of SO_2. The SO_3 formed may possibly precipitate Ba or Sr in this group.

4. Test part of filtrate immediately by adding excess of H_2S (and diluting if gas is used, if strongly acid *partially* neutralize first with NH_4HO), should a pp fall treat the whole in the same way and repeat till precipitation is complete. If amount of pp II is excessive too much of the original substance may have been taken, in such a case the filtrate may be divided at this point, and the pp mixed and then divided for treatment.

5. H_2S must be boiled off or NH_4HO will pp FeS, NiS, etc., here, it will also retard oxidation of Fe″ by HNO_3.

If neither HCl nor H_2S gives any pp, and CrO_3 and MnO_3 are absent a fresh portion may be taken for treatment at this point.

6. Evaporation to dryness may in many cases be omited, but it is desirable to concentrate and reduce bulk after the necessary dilution in §II.

HNO_3 must be added to peroxidize the Fe″ (unless it is intended to add NH_4HO and $(NH_4)_2S$ without intermediate filtration) for ferrous salts are not completely ppd by ammonia.

Evaporation to dryness with conc. HNO_3 is generally necessary in the presence of phosphates, borates, oxalates, fluorides and silicates if NH_4HO gives a precipitate at this point, and always in presence of organic matter which retards or prevents precipitation of Fe (Al and Cr) by NH_4HO. Borates oxalates and fluorides are largely decomposed by this treatment; soluble silicates and organic matter are decomposed (leaving SiO_2 and C); if not removed CaF_2, $Si(HO)_4$, CaC_2O_4, etc., would come down in the place of $Al_2(HO)_6$ on adding ammonia. Phosphates are converted into orthophosphates (H_3PO_4 salts).

7. If heating is carried too far Al_2O_3 white, Cr_2O_3 green, Fe_2O_3 brown or black, will be rendered insoluble in HCl.

8. Pink color changing to blue near dryness indicates Co; green, leaving yellowish residue Ni, green residue Cr, yellow to brown or black Fe, pink to brown Mn.

9. Phosphoric acid must be tested for here, after removal of As and SiO_2 which also give yellow pps with molybdate: a yellow *color* without pp is not sufficient to prove its presence.

If P_2O_5 is present *and* NH_4HO gives a precipitate, special treatment will probably be necessary for the pp No. III.

[This may be often avoided, unless much P_2O_5 be present, by adding a sufficient quantity of Fe_2Cl_6 at this point (after testing for Fe in a special portion), the P_2O_5 being carried down in combination with the Fe on addition of ammonia.]

10. The amount of NH_4Cl necessary depends most on that of the Mg and Mn to be retained in solution as double chlorides after addition of ammonia, and partly on the Ni Co and Zn. If solution has not been evaporated to dryness it usually contains much HCl, which with ammonia forms sufficient NH_4Cl. Too much salammoniac may prevent precipitation of lime group.

11. Too great excess of NH_4HO dissolves $Al_2(HO)_6$ (note 20); the gelatinous almost colorless pp of $Al_2(HO)_6$ must be closely looked for.

12. The ammonia used must contain no carbonate, if exposed to air CO_2 is absorbed so that Ba Sr and Ca may be ppd here and missed in their proper place.

By exposure MnOAq and CoOAq are also oxidized to Mn_2O_3 Aq and Co_2O_3 Aq, becoming insoluble in NH_4Cl and therefore falling in Pp III. Mn (and Co) are usually carried down to some extent if much Fe is present, apparently as Fe_2O_3 MnO; so that if this pp is very large and dark red or brown it is best to redissolve immediately in HCl, reprecipitate hot by NH_4HO, boil, filter and add the filtrate containing Mn (and Co) to the main filtrate, § IV.

Presence of Mn and Co is shown by the pp on filter becoming a *dark* brown. Zn is also carried down by Cr as Cr_2O_3 ZnO, it is but imperfectly separated by reprecipitation.

The ppd hydrates are gelatinous, filtration is tedious and separation from solution imperfect unless performed hot and pp washed with hot water.

The CrO_3 of chromates (and Mn of manganates) is not ppd by NH_4HO. If not previously decomposed by HCl and H_2S it will be ppd by $(NH_4)_2S$; presence is indicated by color of solution.

If solution is pink here some Cr_2O_3 is retained in the ammoniacal solution and must be removed by boiling and filtering (or tested for in pp IV).

14. If Fe has been completely removed in pp III a black pp on adding $(NH_4)_2S$ indicates Ni or Co; Fe if not removed (see notes 6, 7) comes down also as black FeS.

(*b.*) Sometimes the ammonia pp (IV) is not filtered off before adding $(NH_4)_2S$, in this case the method given in the foot-note to the table of separation of the iron groups must be followed: the advantage of filtering it off is that the absence of Ni and Co is indicated at once, and no time need be spent in searching for them afterwards.

15. The ammonium sulphide used should be colorless or only faintly yellow. An excess not only dissolves NiS in presence of NH_4HO, but, especially if yellow, deposits S on heating. Some prefer to pass gaseous H_2S through the ammoniacal solution, keeping it alkaline by addition of NH_4HO.

16. The ppd sulphides, especially NiS and CoS, readily oxidize when moist to soluble sulphates, and may be missed in the group separation, which should be carried on as soon as possible. H_2S prevents oxidization.

17. If filtrate is *brown* Ni is indicated; if so boil for some time, best with addition of a little acetic acid; filter off the NiS + S which falls and test in borax bead OF (oxidize well to get rid of S); it need not be added to main pp (IV).

18. $CaCO_3$ and $BaCO_3$ are *somewhat* soluble in NH_4Cl.

If a large excess of ammonic salts is present evaporate to dryness and ignite to expel them, dissolve residue in dilute HCl, filter off any slight residue, add a little NH_4Cl and make alkaline with NH_4HO. If a white pp forms filter, dry, and test with $Co(NO_3)_2$ for Al or Mg.

19. Solution must be alkaline and NH_4Cl present to keep Mg in solution. If acid, CO_2 would be liberated on adding $(NH_4)_2CO_3$ and a soluble bicarbonate of Ca, etc., possibly formed.

The ammonium carbonate used should be free from bicarbonate (prepared by adding NH_4HO to a strong solution of the commercial salt).

20. Boiling may reconvert $CaCO_3 + 2NH_4Cl$ into soluble $CaCl_2$ and $(NH_4)_2CO_3$ or $NH_3 + CO_2$ which volatilize. (See 21.)

21. Whether $(NH_4)_2CO_3$ gives a pp or not, Ba and Ca may be in this solution, hence a few drops of ammonium sulphate and oxalate should be added to remove them, pp may be subjected to flame test.

If much ammonic salt be present these traces of Ba and Ca are best removed after ignition and before testing for Mg (see separation of Mg Na and K).

N. B.—In every group note carefully the colors and amounts of the precipitates thrown down and what is indicated thereby; by close observation one can often avoid the trouble of separating some of the groups.

22. If silver group pp is large take a portion in test tube, add 5 ccs water and boil, if entirely soluble it consists of $PbCl_2$ only; if not proceed as directed.

Traces of silver are likely to be missed, AgCl is slightly soluble in a solution of $PbCl_2$.

23. The color of the pp thrown down by H_2S often indicates what metals are present, but the different sulphides may mask one anothers color.

If very large a *portion* of pp should be taken to test for As group; but before dividing it must be well mixed. It wlll often be noted that the colors of different portions differ greatly.

24. CuS is slightly soluble in $(NH_4)_2S$ and HgS in K_2S, hence it is preferable to use KHO in presence of Cu and $(NH_4)_2S$ in presence of Hg, or to test original solution for Cu by means of iron.

The $(NH_4)_2S$ should be yellow, containing some polysulphide, so as to convert insoluble SnS into soluble SnS_2. If too strongly yellow so much S will be ppd on acidulating that a small amount of As or Sn will be completely masked (test reagent with HCl); if the pp does not mass together on boiling the As group is probably absent. If the As group is very heavy it may be well to repeat treatment of the residue to insure complete separation.

CuS is ppd from $(NH_4)_2S_x$ of a liver or brown color, may be neglected.

If Sn^{IV} and Hg occur together the Sn is incompletely separated from Hg by these means.

25. In very many places time will be saved by thus testing portions of heavy pps or bulky solutions, but it must be remembered that the quantity of the substance thus taken is proportionately reduced.

26. Excess of acid has to be boiled off or neutralized later; the action of HNO_3 on sulphides yields nitrates, NO, water and S; the S is derived from the H_2S used and not from original substance.

27. A white substance here may be $PbSO_4$, or $BaSO_4$, as well as $Hg_2S(NO_3)_2$, the latter dissolves in Aqua regia like HgS. S is recognized by its burning readily with little or no residue, if plastic it may contain HgS.

28. A small portion may be diluted and saturated with H_2S, if no pp no metals need be looked for (see note 23).

29. The Bi pp must be carefully looked for and confirmed: if Pb is not completely removed it comes down here as $Pb(HO)_2$.

Sb, if not removed, may come down here; SbOCl is soluble in tartaric acid.

30. If solution is not blue test for Cu with K_4FeCy_6, the brown pp is a more delicate test than the blue color of cuprammonium sulphate.

31. A brown or black pp shows that Pb or some other metal has been imperfectly separated.

32. Normal ammonium carbonate dissolves Sb somewhat, in the acid carbonates As is alone soluble: solution is accompanied by escape of CO_2.

33 If H_2S is not driven off Sb_2S_3 is reformed on dilution or cooling.

34. Some of the Sb passes off as SbH_3, especially if much free acid is present. Sn may be ppd on platinum but always as a grey sponge, Sb alone is brown or plack.

35. If long boiled the $SnCl_2$ may oxidize to $SnCl_4$ which does not react.

36. Pp may be dissolved in aqua regia and Marsh's test applied to it or original solution.

37. If colorless contains no Fe or Cr.

38. NH_4Cl added to the KHO solution also pps Al: Al may be confirmed by blue color produced by moistening pp with $Co(NO_2)_3$ drying and igniting. A little Al may come from reagents, especially KHO, or from vessels used.

39. If blue test for Cr, if yellow this is sufficient proof.

40. NiS and CoS are slightly soluble in HCl, but difficultly even in the strong acid.

41. Ni and Co can be separated by adding KCN till pp formed is just redissolved, boiling for five minutes, when cool filter if necessary, add KHO and then Br water in excess, keep warm for ten minutes, filter, black pp$=Ni_2(HO)_6$. Co remains in solution, dry and test in borax bead.

42. Mn is generally found in Pp III and need not be confirmed here.

43. The Zn pp is easily overlooked, ZnS is the only white sulphide ppd.

44. Compare note 14 (b).

45. In this group all the precipitates should be given ample time to form and settle.

46. See note 21.

47. If Al (Ba or Ca) be present, Na_2HPO_4 gives a floculent noncrystalline pp: this should be treated with acetic acid which dissolves $MgNH_4PO_4$ but not $Al_2(PO_4)_3$, and filtered solution reppd by NH_3HO.

48. The sodium flame is rarely absent, but is persistent if substance contained Na in considerable quantity. See that wire itself does not affect flame.

49. Most of the Ni Co and Zn was retained in solution by NH_4Cl.

50. Absence of P_2O_5 here indicates that sufficient iron was present to combine the whole of it : if found more iron must be added.

The ammonium acetate forms metallic acetates and ammonium chloride.

51. Separate the phosphates in the same way as hydrates in Pp III.

52. It is well to evaporate and get rid of ammonic salts by ignition.

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